

DEVELOPMENT OF A REPRODUCIBLE SCREENING METHOD TO DETERMINE THE MECHANISM AND EFFECT OF ORGANIC ACIDS AND OTHER CONTAMINANTS ON THE CORROSION OF ALUMINUM-FINDED COPPER-TUBE HEAT EXCHANGE COILS

Final Report

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EXECUTIVE SUMMARY

Formicary Corrosion

Formicary corrosion is an insidious form of localized pitting corrosion. Notoya (1997b) wrote, "In Japan, this type of corrosion is found in approximately 10% of cases of premature failure of copper tubes." Attack characteristically features very small surface pits which are not visible to the un-aided eye, and random directional changes in the underlying copper metal. Attack is rapid. Failures have occurred before installation, shortly thereafter, or within several years later.

Objectives of this Research Project

Conduct an in depth literature search on the subject of formicary corrosion.

Define the corrosion mechanism.

Develop a test method that will reproduce formicary corrosion.

Develop a test method for screening candidate materials that could cause formicary corrosion.

Results

Literature Search

The approach adopted relied on a review of work conducted on formicary corrosion, methods used to assess the damage, and corrosion mechanisms proposed. Most of this work was conducted since the late 1980's, principally in Japan. More than sixty papers were obtained and reviewed (three of these papers were written or cowritten by the lead author of this project, Richard A. Corbett).

Failure analyses and laboratory tests provided a growing list of agents known to cause formicary corrosion. Initial interest focused on chemicals used to clean and/or lubricate copper tubing during the manufacturing and assembly processes. The decomposition of susceptible chemicals, usually by hydrolysis, produced organic acids (such as formic and acetic acids), which were shown in laboratory tests to cause formicary corrosion, even at very low concentrations (Notoya et al 1988). As discussed later, research into the environment associated with aluminum-finned copper-tube heat exchanger coils, both residential and commercial/industrial, indicated that the accumulation and breakdown of vapors and condensation produced organic acids. The vapor phase was found to be the most critical in inducing formicary corrosion.

Notoya (1991a,c,d) has developed procedures to protect the inside surface of the copper tubes from formicary corrosion by steam cleaning, drying, and sealing them. The outside surface can be protected if it is carefully cleaned and kept dry. Some coatings with an inhibitor have shown promise. Miyafuji (1995) has reported tests on an alloy (copper with two percent manganese) that looked promising.

The corrosion mechanism

Various formicary corrosion mechanisms have been proposed by a number of researchers. Notoya's theory is the most widely referenced in the literature. This project does not invalidate any of the corrosion mechanisms discussed. The studies undertaken in this project have provided a better understanding of the mechanisms of formicary corrosion. It is now established that formic acid causes a branch-like "tunneling" that initiates in grain boundaries of the copper metal; acetic acid tends to display a more general dissolution in the metal matrix.

The test method

The test method developed in the present studies is based on previous work by Notoya, (Notoya et al 1989) who has contributed significantly to a better understanding and awareness of formicary corrosion. The proposed test method not only provides an opportunity to screen fluids that may be causative of formicary corrosion, it can also be used to determine the susceptibility of copper (or coated copper) to attack. The basic test setup is a one liter glass container that has a length of copper tubing suspended above a 100mL aliquot of test fluid. The container is thermally cycled so that the some of the test fluid evaporates and then condenses on the copper tube. The condensate may then produces formicary corrosion.

Laboratory tests were conducted on various organic acids (including different concentrations of formic and acetic acids) to develop a screening test that would display formicary corrosion over relatively short term exposures. These tests provided times, temperatures, and fluid concentrations for the ultimate screening test proposed. These studies were augmented with metallographic assessments to determine the nature and extent of formicary corrosion that occurred.

A statistical analysis of the formicary exposure tests undertaken for this project ranked the input variables in the following order of importance to formicary pit depth:

- log concentration of the acids (a higher concentration had more aggressive attack)
- the inverse proportion of acetic acid (formic acid was more aggressive than acetic acid)
- the high temperature (T-hi) (40°C was more aggressive than 55°C)
- the low temperature (T-low) (20°C was generally more aggressive than 4°C)
- the length of exposure (in days) (The longer the exposure the deeper the formicary pits).

In the case of formic acid, the threshold for formicary attack was below twenty (20) parts per million (ppm).

The screening test

The research effort described in this report was expanded to develop a reproducible laboratory test method that would investigate the effect of organic acids and other contaminants on the corrosion of aluminum-finned copper tube heat exchangers. Specifically, the intention was to

provide a test method to determine the propensity of candidate fluids to cause formicary corrosion. In parallel work, studies focused on procedures for analyzing candidate fluids using a combination of infrared (FTIR) and ion chromatography (IC) analytical techniques. The ultimate recommendation involves the analysis of hydrolyzed fluids using IC.

This proposed test matrix will find major application in screening candidate fluids used for forming, fabricating, joining, and insulating heat exchanger coils. The procedure involves a preliminary conditioning of the fluid (e.g. hydrolysis or thermal dissociation), an analysis for carboxylic species (IC or FTIR), and a laboratory exposure to vapors derived from the subject fluid for a period of up to three months. If present, formicary corrosion attack is confirmed and monitored using conventional optical microscopy. The test methods developed and used in this project have provided a satisfactory screening test.

Nomenclature

Organizations

ARTI	Air-Conditioning and Refrigeration Technology Institute
CTL	Corrosion Testing Laboratories, Inc.
JCDA	Japan Copper Development Association
UNS	Unified Numbering System [for alloys]

Analysis Methods

EPMA	electron probe microanalysis
FTIR	Fourier Transform Infrared spectroscopy
IC	ion chromatography
SEM	scanning electron microscope
XRD	x-ray diffraction

Corrosion Terms

Corrosion: An electrochemical attack on a metal, evidenced by mass loss and/or changes in properties.

Pitting: A nonuniform type of corrosion where microcells develop as discrete holes in a metal. Usually quite aggressive and leads to unexpected failure.

Formicary corrosion: Micro-pitting corrosion in copper with an unusual branching morphology. Looks similar to the cross section of an “ants’ nest” (i.e., a formicary). Also called “ants’ nest corrosion.”

Intergranular corrosion: Corrosion that proceeds along the grain boundaries of a metal.

Copper Terminology

JIS H3300 (UNS C12200): JIS is Japanese Industrial Standards, H deals with nonferrous metals, 3300 deals with seamless copper and copper alloy pipes and tubes. (UNS is the Unified Numbering System, C is copper, and UNS C12200 includes some silver and is a

phosphorous deoxidized, high residual phosphorous copper. The phosphorous deoxidizes the copper by forming phosphorous pentoxide. The UNS 5 digit system is based on the older Copper Development Association (CDA) 3 digit system. For example, UNS C12200 is sometimes seen as C122 or CDA 122. The Japanese sometimes use a 4 digit system, where C1220 would be comparable to UNS C12200.

JIS H3200: welded copper and copper alloy pipes and tubes.

DHP: **D**eoxygenated **H**igh residual **P**hosphorous content copper, such as UNS C12200 or UNS C12300

DLP: **D**eoxygenated **L**ow residual **P**hosphorous content copper, such as UNS C12000 or UNS C12100

OF: Is an **O**xxygen **F**ree copper, such as UNS C10200.

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Development of a Reproducible Screening Method to Determine the Mechanism and Effect of Organic Acids and other Contaminants on the Corrosion of Aluminum-finned Copper-tube Heat Exchanger Coils

1. INTRODUCTION

Formicary corrosion is an insidious type of pitting most commonly found in copper tubing used in aluminum-finned copper-tube heat exchanger coils/tubes. Attack is usually rapid. Pitting is so fine it must be magnified to be seen. There is typically little, if any, corrosion product at the opening of the pit, and the tube is usually discolored in this area. Formicary corrosion is generally typified by substrate attack comprising branching tunnels with random direction changes.

The similarity between this morphology and the appearance of an ants' nest led Yamauchi et al (1983) to label it formicary; a formicary is defined as an ants' nest. Later, Notoya and Hammamoto (1990) popularized the term "Ants' nest corrosion". It is a serendipitous coincidence (Sato 2001) that formic acid, which John Ray first isolated in 1671 from the bodies of dead ants, causes formicary corrosion.

Copper tubing is widely used in heat exchangers (such as industrial chiller units, commercial refrigerators and unitary home air conditioning units) around the world. The popularity of copper is ascribed to its excellent heat conductance and its malleability. Nagata and Kawano (1994) note that the production of air conditioner units greatly increased in the late 1970's. Notoya (1997b) estimated that in Japan, 10% of the premature failures of copper tubing used in various types of heat exchangers are attributable to formicary corrosion. Interest in this very costly problem has grown rapidly since the mid 1980s.

This commissioned project consisted of a literature review of approximately 60-papers, which revealed a range of failure analyses, identified the development and refinement of procedures to duplicate formicary corrosion in the laboratory, recommended preventive measures, and provided an understanding of various corrosion mechanisms. The majority of this prior research was undertaken in Japan, beginning in 1983.

As the result of the literature search, a laboratory testing program was developed to obtain reproducible results, which could be used as a screening method for formicary corrosion. The ultimate screening test involved the analysis of hydrolyzed fluid with subsequent exposure to vapors in a controlled laboratory test.

A six-month (182-day) exposure test used solutions of formic acid, acetic acid, a 20% formic acid 80% acetic acid mixture, and ethylene glycol extracts. These solutions were tested at three different temperature cycles (55/20°C, 40/20°C, and 40/4°C). The cycle was at the higher temperature during the 63-hours of the weekend and the 15-hours of each weekday night. The cycle was at the lower temperature for the 9-hours of each weekday day. Further, the acid solutions were tested at three different concentrations (10,000-ppm, 1,000-ppm, 100-ppm); deionized water was used as a control at the three temperature cycles.

A 50-day exposure test focused on the most aggressive conditions determined from the longer six month test (i.e. formic acid at the 40/20°C temperature cycle [15-hours/9-hours + 63-hours]). Three different concentrations were tested (100-ppm, 50-ppm, and 20-ppm) to see if a threshold value for initiation of formicary corrosion could be determined. Duplicates were run to determine the repeatability and reproducibility of the testing method.

As a variant of the test program, blindly submitted fluids were subjected to thermal degradation and hydrolysis prior to analysis by ion chromatography (IC) for levels of formic and acetic acids. Such a test represents a screening method for process fluids.

2. SUMMARY OF FORMICARY CORROSION LITERATURE REVIEW

(For additional detail see Appendix F)

An extensive literature search showed that instances of formicary corrosion may have been recorded, but not recognized as such, in the 1940's (Evans 1960). Specific references to formicary corrosion appeared from the 1960's to the present, notably in Japan where studies were complimented by surveys conducted in collaboration with the Japanese Copper Development Association (JCDA).

The literature search served two primary purposes. First, the review considered sources and causes of formicary corrosion as revealed from failure analyses. Second, the search provided information about laboratory procedures that were used to study and duplicate formicary corrosion.

Notoya (1990) has drawn attention to certain common morphological similarities to "keloid" corrosion in Be-Cu alloys, "red plug" corrosion in silver-plated copper wires, "directional pitting" in Alloy 20, and "bronze disease." In the late 1940's Evans (1960) analyzed and treated museum artifacts that had displayed "bronze disease" following exposure to acetic acid vapors from wood shavings.

2.1. Failure Analysis Studies

Failure analysis studies have generally identified residual organic compounds, including anti-freeze solutions used for storage, lubrication fluids used in manufacturing, cleaning chemicals used before and during service, certain adhesives or insulation materials, and some foodstuffs as primary sources of formicary attack when the organic substance breaks down to form carboxylic acids, such as acetic and formic acids. The literature survey refers to well over 100 cases (Isobe 1992) of formicary corrosion failures.

Studies involving phosphorous deoxidized copper (UNS C12200) tubing have continued for over 35 years. The summary findings are that most attack (approximately 60%) starts along the outside tube surfaces compared with approximately 34% along the inner surfaces. Failures are more commonly reported (approximately 66%) along straight lengths of tubing than in bent sections. Failures are typically attributed to residual organic substances that were inadvertently left inside or outside manufactured tubing, or to fluids that contain chemicals that are now known to dissociate and cause formicary corrosion (braze fluxes, solders, and acid foodstuffs (Isobe et al 1992, Elliott and Corbett 1999).

2.2. Laboratory Testing Procedures

The literature search provided a historical perspective on laboratory testing methods adopted primarily in Japan by Notoya and his co-workers. Two basic experimental procedures were developed. The first test involved short straight lengths of copper tube exposed to vapors developed from the subject fluid (Notoya et al 1989). The second test placed the subject fluid

inside a hairpin formed copper tube. Tests were conducted from about a week to several months at ambient (or higher) temperatures. In some tests the temperature was raised to 150-400°C, to simulate brazing conditions (Notoya et al 1988).

The laboratory tests typically employed one liter sized glass containers with 100-mL of the subject fluid. Tests have been conducted primarily on UNS C12200 copper and have explored the effects of many environments, including solvents (Hammamoto and Imai 1991), evaporative and nonevaporative oils (Takahashi et al 1992), drawing and finning fluids (Corbett and Elliott 2000), carboxylic solvents and organic solvents ((Notoya et al 1989), alcohols, aldehydes (Notoya 1997c), vinegar and other food stuffs (Notoya, 1997d), and chemicals associated with woods and wood paneling (Notoya 1999).

Current procedures for testing, which were taken into account in developing the screening test for the ARTI program, include pre-hydrolysis of subject fluids with subsequent exposure trials for up to several months with fluids that contain carboxylic species. The laboratory tests reviewed showed that cyclical temperatures exacerbated formicary corrosion (Isobe et al 1992). Fluoro-rubber and silicon rubber seals were speculated to cause formicary corrosion and should be avoided in laboratory testing. (Isobe 1992)

The test developed for this program (see Section IV) relied upon a pre-hydrolysis (for the ethylene glycols) or preparation of test solutions using reagent grade formic and acetic acids with deionized water. The solutions were analyzed by IC with subsequent exposure for up to six months in vapors derived from the subject fluids. Optical microscopy was used to assess the extent or otherwise of formicary corrosion.

2.3. Preventive Measures

Formicary corrosion cannot occur without the simultaneous presence of oxygen, water, and a specific organic compound that is able to dissociate and produce carboxylic acids. In the ideal world, eliminating any one of these parameters will prevent formicary corrosion; in reality, because the phenomenon is not so widely known or recognized, material or chemical approaches that mitigate the problem are typically considered.

The literature search summarizes work done in Japan and elsewhere on improved cleaning methods, inhibitors, coatings, and alternative copper alloys. Dry clean copper tubes free from organic compounds are recommended (Notoya et al 1989). Inhibited surfaces have been studied (Notoya et al 1989) and testing has shown that certain azoles are relatively effective in resisting formicary corrosion. BTA (1,2,3-benzotriazole) and UDI (2-undecylimidazole) have shown particular promise in laboratory trials. Several proprietary products, including some epoxy coatings, are cited as potential ways to reduce formicary corrosion (Notoya 1991 a, c, d; 2001a).

Of several copper alloys that were studied, a Cu/2% Mn alloy out performed others in that only marginal formicary attack was observed after tests that lasted up to 40 days (Miyafuji et al 1995). Formicary corrosion was not prevented, only minimized.

3. THE FORMICARY CORROSION MECHANISM

The generally accepted mechanisms for formicary corrosion are based on the models advanced by Notoya in Japan. The following paragraphs summarize the method by which basic theories have changed in recent years. The majority of studies consider the role of copper complexes (carboxylates) with different cathodic reactions.

3.1. Notoya's Mechanism

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

Yamauchi et al (1983) 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 corrodent.

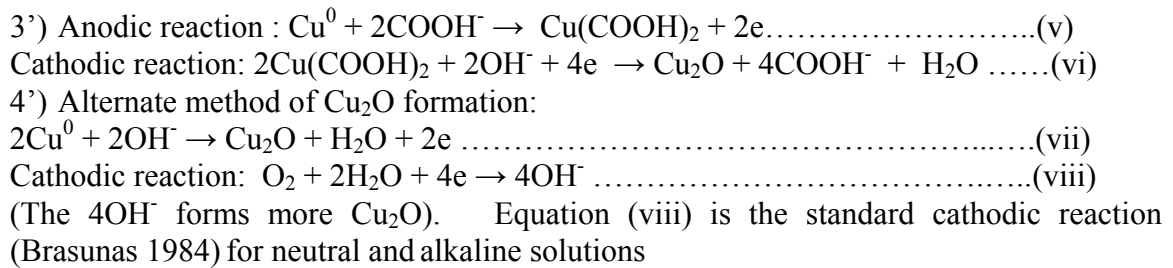
Notoya et al (1988) reported formicary corrosion from laboratory tests with four different carboxylic acids, the most aggressive being formic acid. Their equations of reaction and explanations have been widely adopted; a slightly modified version of the original mechanism is provided here:

- 1) Weaknesses, such as discontinuities in the oxide film, allow access by the organic carboxylic acid present:
- 2) The copper oxidizes (corrodes)
$$\text{Cu}^0 \rightarrow \text{Cu}^+ + \text{e} \dots \dots \dots \text{(i)}$$
- 3) Carboxylic acid ions and copper anions form a copper complex:
$$\text{Cu}^+ + \text{X}^- \rightarrow \text{Cu}(\text{X}) \dots \dots \dots \text{(ii)}$$

(Where X is the selected carboxylic acid)
- 4) The copper complex is oxidized to form cupric oxide (Cu₂O) and copper carboxylate:
$$4\text{CuX} + \frac{1}{2} \text{O}_2 \rightarrow \text{Cu}_2\text{O} + 2\text{Cu}(\text{X}_2) \dots \dots \dots \text{(iii)}$$
- 5) Micro cracks are formed in the pit wall due to the volume expansion of the Cu₂O
- 6) The formed copper carboxylate complex reacts with the pristine crack surfaces and the cuprous complex reforms:
$$\text{Cu}(\text{X}_2) + \text{Cu}^0 \rightarrow 2\text{Cu}(\text{X}) \dots \dots \dots \text{(iv)}$$

These reactions then recur and are autocatalytic.

Notoya (1991c) introduced some alternate equations of reaction to 3) and 4) above, and included the corresponding cathodic reactions (using formic acid instead of the generic X as first stated):



Notoya (1992) considered the standard (Brasunas 1984) cathodic reaction in acidic solutions:
 $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \dots\dots\dots(\text{ix})$

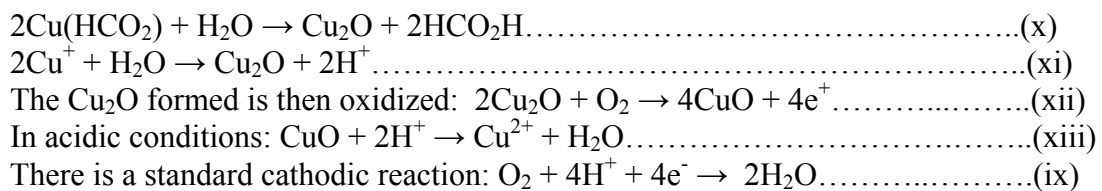
Equations of reaction (i-iii) and the cathodic reaction (ix) for an acidic solution were still current in Notoya's (2001c) more recent work.

3.2. Responses to Notoya's Mechanism

Miya et al (1993) presented a theory, first proposed by Matsuoka, based on capillary action drawing water into the pit with surface tension effects at the mouth of the pit. Notoya et al (1989) accepted capillary force as an explanation for water transport and how pits can proceed in a direction opposite to gravity, but argued that condensation inside the pits may be equally valid. Notoya suggested cyclic heating works as a pump to bring oxygen and water vapor into the pit.

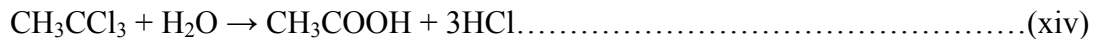
Miya suggested that capillary action does not account for the observation that corrosion products are more prevalent deeper inside the pit. The absence of copper formate and carbon inside the pit, as evidenced by SEM and EPMA work, weakens the mechanism for equations (ii) and (iii) above. While admitting the solubility of copper formate in the water used for polishing the metallographic specimens, Miya does not accept that all traces of the copper formate should have disappeared. He proposes alternate equations of reaction involving the presence of formic acid in a spongy Cu_2O product without a copper formate complex.

Miya suggests two alternate methods to account for Cu_2O formation (versus Notoya's reaction equation (iii)):

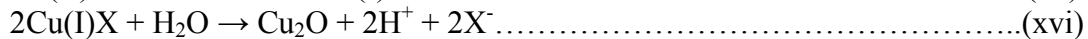


Miya suggests that traces of formic acid that were not removed during polishing were evaporated in the SEM when the vacuum was drawn. He proposes that the tunnel morphology is related to the amount of water present at the mouth of the pit: a small amount of water forms a narrow tunnel and a larger amount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

Nagata and Kawano (1994) proposed an equation of reaction for the hydrolysis of 1,1,1-trichloroethane to acetic acid:

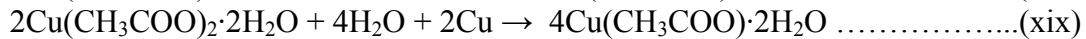
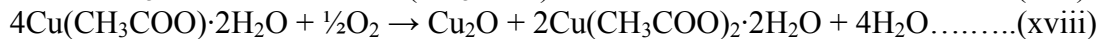
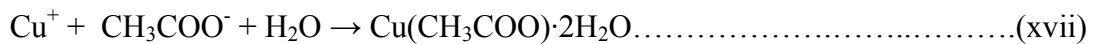


Baba and Kodama (1995) produced potential-pH (*E*-pH) diagrams for copper with acetate and formate solutions. Using XRD and FTIR they were unable to find Cu(I)X complexes in their work, but said this might be an issue of concentration; they note that their mechanism is similar to Notoya's.



The tunneling was accounted for by activation at the advancing pit front with passivation on the pit walls. Notoya (1997a) perceived their thermodynamic work as a validation of his mechanism.

Cano et al (1999) applied Notoya's equations of reaction to acetic acid and included hydrates in their considerations:



Equations (xviii) and (xix) are autocatalytic and recur. The main cathodic reaction (a standard formula) is that for neutral and alkaline solutions, as noted earlier:

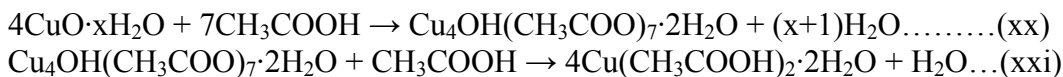


3.3. Other Investigations

Lopez et al (1998) reported studies on copper corrosion caused by exposure to small concentrations of acetic acid vapor. The focus was on the development of copper patinas in the atmosphere, but their research was interesting and applied to formicary corrosion. Phosphorous deoxidized copper plates (UNS C12000) were exposed to 5 different 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 acetic acid in the vapor phase, which

roughly correspond to levels of 600, 3,000, 6,000, 12,000, and 18,000-ppm respectively in the test solutions (by comparison with the studies done by other researchers mentioned earlier, 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. The concentrations they used would have produced formicary corrosion.

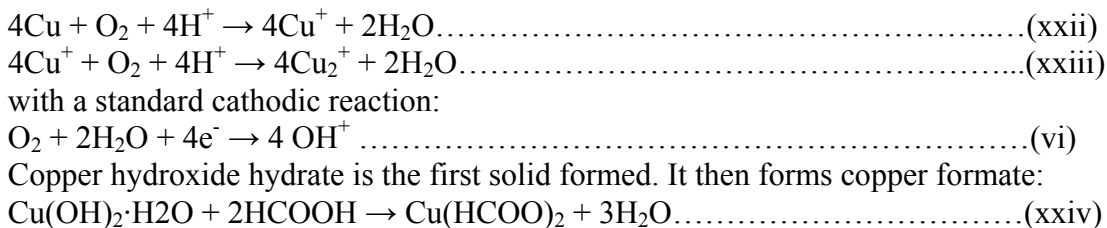
The descriptions and photographs of the plates exposed by Lopez are quite applicable to the corrosion products on the outside of tubes exposed to acetic acid vapors. They proposed the following equations of reaction for the formation of copper hydroxide acetate and copper acetate which they found:



Lopez suggests 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 copper surface.

Bastidas et al (2000), published a patination study using formic acid with the same experimental conditions and analytical techniques as noted above for acetic acid. They used triplicate samples and reported a reproducibility of over 95%. The vapor concentrations of 10, 50 100, 200, and 300-ppm formic acid roughly correspond to test solution concentrations of 140, 700, 1,400, 2,800, and 4,200-ppm, respectively. (These concentrations are different from the acetic solution concentrations noted above because formic acid and acetic acid have different vapor pressures.)

Bastidas proposed that the formic acid might act as a catalyst for initiating corrosion.



At low levels (10 and 50-ppm, vapor) the XRD shows copper hydroxyformate, which may form via:



Notoya was then mentioned and three of his equations of reaction presented (the first and last slightly modified) as an alternate way to get cuprite.



The maximum corrosion rate was 13-mdd. As with the acetic acid tests, apparently no cross sections were made; formicary corrosion was not reported.

Corbett (2004) proposed 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. Notoya's mechanism is accepted, but the testing for this project, especially the fifty day test where intergranular attack was frequently observed, lead to the inclusion of intergranular attack in the mechanism 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 (Cu_2O) and cupric formate:



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



These reactions, (xxix) and (xxx), 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 [$\text{Cu}(\text{COOH})_2 \cdot 4\text{H}_2\text{O}$]. It is proposed that intergranular attack is present and is the operative force in the apparently random directional changes typical of formicary corrosion even when intergranular attack is not obvious on a metallographic cross-section. Higher concentrations of formic acid are believed to obliterate the evidence of intergranular attack due to rapid grain dissolution.

4. A FORMICARY CORROSION TEST METHOD

4.1. Procedure

The procedure used in the exposure tests developed at Corrosion Testing Laboratories (CTL) was that developed by Notoya (1997d, et al 1989,) which has been popular among Japanese researchers. The procedure used:

- A closed glass test vessel of about 1-L volume
- 100-mL of solute
- A section of copper tubing exposed to the vapor from the solute
- Thermal cycling

A more detailed discussion of the formicary test procedures used is contained in Appendix A: Formicary Testing Procedure. The principal points and some differences between the six month and fifty day tests are covered here.

4.1.1. Test Setup

The formicary tests were undertaken using alloy UNS C12200 copper tubing obtained from a single manufacturer. The tubes were approximately 3/8-inch in diameter with a minimum wall thickness of approximately 12-mils (a mil is 0.001-inch); they were welded and annealed.

The tubes were cut to lengths between 5-cm and 6.4-cm and each was engraved with an identifying number prior to cleaning with methanol and acetone and drying with a heat gun. The tubes were handled with nitrile gloves during and subsequent to cleaning.

For the six-month test the test vessels were 32-ounce [~1-L] glass jars with lids that had cardboard inserts adhered to a TFE (Teflon™ type) lining. In the fifty-day test the test vessels were one-liter glass jars with a wire bale and a rubber gasket (old style canning jars). A piece of polyethylene film was used to isolate the gasket from the test vapor in the fifty-day test. A test was done on the polyethylene film to determine that it would not contaminate the test. Both types of jars employed were new and each was rinsed three times with deionized water and allowed to air dry before to use.

The copper tubes were suspended well above the level of the test solution at about a 45° angle near the top of the test vessels using a length of PTFE string. An advantage of the wire bale type jar was that the tube would remain where placed when the hinged lid was closed. The screw-on lid would pull on the string, altering the angle and position of the tubes.

In the six-month test the tubes were lifted out of the jars while the 100-mL test solution was poured into the test vessel. In the fifty-day test this was not found to be necessary as a long necked funnel was used. For the six-month test, the jars were purged with oxygen for a minute at the start of the test and after the first section was cut from the tubes (between day 14 and day 52), but not after subsequent sectioning; no oxygen purge was done in the fifty-day test.

Japanese researchers typically reported solute concentrations as volume percent but CTL used mass. The formicary testing procedure normally used a solution of formic acid to successfully initiate formicary corrosion. However, it was reported that on drip pans under condenser units which had been found to have formicary corrosion there was a ratio of 20% formic acid and 80% acetic acid. Subsequent tests in the six month study included an acid mixture in this ratio, and acetic acid by itself.

In the six month study the acid solutions were carefully prepared and samples of the solutions were kept for possible future confirmation of acid concentrations. By the time the fifty day study was initiated it had become standard practice to test the acid concentrations using IC, and to adjust as needed, before the test began.

Three different extracts of ethylene glycol were included in the six month study. First, a 100-mL sample of ethylene glycol was thermally degraded in a Teflon container at 196°C for an hour in the presence of a cleaned piece of aluminum finning and copper tubing. A Fourier Transform Infra-red (FTIR) analysis was done, which revealed the generation of carboxylic acid. The sample was then mixed with 200-mL of deionized water and analyzed by IC to determine the concentration of formates. Second, for hydrolysis, 180-mL of ethylene glycol was mixed with 20-mL of deionized water and heat refluxed in an erlenmeyer flask, which was heated to boiling and condensed for a period of 48-hours in the presence of pieces of corroded aluminum finning. This solution was then mixed with 180-mL of deionized water and analyzed by IC. Third, a new hydrolysis was performed as above except using uncorroded aluminum finning. The hydrolysis procedure used was based on that reported by Hamamoto and Imai (1991).

4.1.2. Test Conditions

Each test vessel was run at one of three temperature cycles: 55°C/20°C, 40°C/20°C, and 40°C/4°C. The test vessels were kept in an oven at the high temperature overnight and over weekends. During the 5 nine-hour days (8 am to 5 pm) of the workweek, the ovens were turned off and the door was opened to allow the test vessels to cool to ambient temperature, around 20°C. In the case of the 40/4°C cycle, during the day, the test vessels were removed from the oven and placed in a refrigerator. Ignoring the time needed for heat up and cool down, the test vessels were at the high temperature about 73% of the time, and at the low temperature for about 27% of the time. During the heating period some of the test solution evaporated, and during cooling it condensed. Some of the condensate formed on the copper tubes and caused formicary corrosion.

The six month test involved 39 test vessels:

1. Three acid solutions at three concentrations for three temperature cycles (27 test vessels)
2. Three ethylene glycol extracts for three temperature cycles (9 test vessels)
3. Deionized water control for three temperature cycles (three test vessels)

4.1.3. Evaluation

It was planned to remove a tube for sectioning once visual observation through the glass showed evidence that corrosive attack was occurring (as evidenced by the tube browning or the solution changing color). A section approximately 6-mm to 9-mm long was removed for metallographic mounting from the top of the tube using a cleaned diamond saw. The remainder of the copper tube was returned to the test vessel. After all of the iterations were initially sectioned (between 14 and 52-days), subsequent sections were done at the same time (seventy-days and six-months) for samples from almost all of the test vessels.

Because multiple sectionings were planned, each test vessel had two lengths of copper tube in it with two exceptions. The three test vessels that had 10,000-ppm of formic acid had only one copper tube because past experience indicated that significant formicary attack would quickly develop. It was thought that this iteration would only have to be sectioned once to confirm that the test was progressing normally. Through-wall penetration was expected well before 70-days.

In retrospect, as discovered by post testing statistical analysis, it would have been better for the test matrix to section the copper tubes in 10,000-ppm formic acid at seventy-days and six-months. The three test vessels which contained the deionized water control had only one copper tube because only one sectioning was also planned for this iteration, at the end of the six-month test.

At the end of the six-month test some copper tubes were evaluated at sections cut from the middle or bottom of the tube. This evaluation endorsed observations made previously by CTL that the most aggressive attack occurred near to the top of the tube.

In the fifty-day test there was only one copper tube per test vessel, and each test vessel was opened only once, when it was taken off test. There were three concentrations of formic acid (100-ppm, 50-ppm and 20-ppm) for 5 ten-day time periods with duplicate tests giving a total of 30 test vessels. Six test vessels were opened every ten-days, the copper tubes were removed, and a section was prepared and evaluated from the top of each tube. The mounts were then ground and polished two additional times so that every mount had data from three successive locations.

4.2. RESULTS

The results of the metallographic examination for the six-month test are in Tables 1 – 5 in Appendix B: Tables of Test Results. The results of the fifty-day testing are in Tables 6 and 7 in Appendix B.

The deepest pits visible on the outside surface of each tube cross section were determined for both the six-month and fifty-day tests using the reticule on a metallograph. The depth of the deepest pit and an average of the five deepest pits were recorded.

Attack on the inside surface of the tubes was ignored except for two situations: (1) involving tests with ethylene glycol where it was difficult to find attack, where blue spots on the inside surface were examined, and (2) on tubes exposed to 10,000-ppm formic/acetic or acetic acids which displayed such a large amount of general corrosion that the original tube boundaries were no longer visible.

The minimum amount of remaining metal was measured on the following 4 six-month tubes: the 40/20°C 10,000-ppm formic/acetic tube and all of the 10,000-ppm acetic tubes. These assessments included attack from both the inside and outside of the tubes. On the seventy-day tubes removed from the same solutions, the deepest pit was measured from the current (corroded) outside edge, implying that there was less corrosion than was actually the case.

The number of pits visible on the outside surface over an arc of the cross section of each copper tube at 25X magnification was recorded, selecting the cross section with the greatest number of pits at the center of the reticule. This arc extended around about one third of the tube circumference. These values were referred to as “pit density” (in Tables 1 – 7). It should be noted that pit density described pits per arc length, not pits per area as usually reported in the literature. It should be noted that pits that were indistinct at 25X magnification were not counted.

The morphology of the formicary pitting was included in the tables and annotated as the “branch ratio.” A pit was considered to be formicary when it had a branched pattern or a classic semi-circular blue pit. The “branch ratio” (number of pits with branching divided by the number of pits with branching and/or a blue color) distinguished between these.

Because the depth of formicary attack could be variable in any given cross section, the mounts were ground to and evaluated at three different depths, except for the initial mounts (14 – 52 days) of the six-month test and the few additional mounts made from sections from the “bottom” and “middle” of the copper tube.

After the conclusion of the six-month test, retained samples of the original three test concentrations of formic acid were analyzed by IC. Post-test samples from the 1000-ppm and 100-ppm formic acid jars and post-test samples of the ethylene glycol extracts were likewise tested. The results of these tests are in Table 8 (Appendix B).

Selected photographs are displayed in Appendix C: Photographs of Corrosion Test Results. Additional photographs of the test specimens are in the accompanying CD. For convenience in reviewing the CD photographs, the CD includes a photograph index with links to modified copies of Tables 1 through 7 (Appendix B), and these tables link to the appropriate photographs of most data points. The tables are set up like a web page; click on the blue underlined text to see the picture.

A statistical analysis has been performed on the data generated from the seventy-day and the six-month mounts (Appendix D: Statistical Report).

4.3. DISCUSSION

4.3.1 Six-Month Testing

Differences in the inputs of the testing (acid type, concentration, and temperature cycle) are apparent (Table 1, Appendix B); The greater the concentration of acid the more aggressive the attack; formic acid was the most aggressive acid; and, the 40/20°C temperature cycle was usually the most aggressive.

The statistical analysis determined that the input variables for maximum pit depth (in descending order of importance) was:

- log concentration of the acids
- the inverse proportion of acetic acid
- the high temperature (T-hi)
- the low temperature (T-low)
- the length of exposure (in days)

The analysis showed that 62% of the variance in the maximum pit depth is accounted for by the five inputs, but this number would increase if input interactions were considered.

This suggests an interaction between the number of days on test and log concentration of acid, but some of this interaction may be due to differences in measuring some of the tubes exposed to 10,000-ppm acetic and formic/ acetic, as mentioned above.

The analysis inferred that the maximum pit depth and the average-of-five pit depth measurements were largely redundant, suggesting that only the two deepest pits should be considered. In addition, it suggested that the pitting density data was statistically less well behaved, and not recommended in future formicary corrosion studies.

The copper tubes in the six 10,000-ppm acid jars showed an orderly progression in maximum formicary depth from the pre-70-day through the 70-day and six month evaluations. However, the same could be said for only four of the nine 1,000-ppm jars, and only one of the nine 100-ppm jars. In five of the 24-acid jars, the deepest pit observed at 182-days was actually shallower than the deepest pit observed at 70-days. Three polishings were thought to be adequate to find a pit reasonably close to, if not absolutely, the deepest. At lower concentrations, this was not always true. It would be prudent to do additional polishes on copper tubes exposed to low-concentration fluids in future testing.

The test solution concentration data shown in Table 8 (Appendix B) showed that the post-test concentrations had fallen to as low as 42% of their original value. Some of this loss was attributed to the corrosion process, and some to the brief jar openings when a tube was removed for sectioning. For the formic acid 1,000-ppm concentrations the trends were inverse to the depth of attack. The 40/20°C cycle had the deepest pitting and the least remaining formic acid, followed by the 40/4°C and the 55/20°C cycles in that order. For the copper tubes exposed to

100-ppm of acid, the order (by temperature cycle) of remaining formic acid was the same, but the tubes exposed to the 40/4°C cycle had deeper pitting than the 40/20°C cycle.

4.3.2. Fifty-Day Testing

The most striking aspect of the fifty-day testing was the aggressive attack observed at low concentrations of 100, 50 and 20-ppm of formic acid. After ten days one of the copper tubes exposed to 100-ppm of formic acid had a depth of attack of 6.1-mils. This was unexpected when compared to the six-month test, where at 14-days the copper tube exposed to 10,000-ppm formic acid at 40/20°C tube had a maximum observed pit of 6.1-mils (abet from only 1 polish). Though at six-months, the maximum depth seen in a copper tube exposed to 100-ppm of formic acid at 40/20°C was 3.0-mils. It was not clear why the 100-ppm formic acid solution appeared to be more aggressive in the fifty-day test. The variable nature of the results implied probable experimental factors that influenced performance, including (but not limited to) jar type and the polyethylene film. A formicary attack depth of 2.1-mils was seen in one of the copper tubes in both the 50 and 20-ppm formic acid concentrations after 10-days.

As noted above, all of the copper tubes were polished to, and evaluated at, three depths. For this reason it was postulated that the pitting depth in the duplicate copper tubes would be fairly close, which was not always the case. In six of the fifteen iterations (three concentrations at five time periods), one of the duplicate copper tubes had from two to five times the observed maximum depth of formicary pitting as the other. Furthermore, there was usually no orderly progression over time in depth of maximum formicary pitting. For example, a copper tube with a maximum observed formicary attack deeper than that found in the 100-ppm, 10-day tube was not seen again until day 40. As discussed above, additional polishing might find deeper pits.

It was hoped that the statistical distribution of pit depths could be represented by three cross-sections per tube. The typical zig-zag morphology of formicary corrosion yields a truism familiar to cavers; the distance traveled to achieve a certain depth may be a multiple of that depth. A few formicary pits were practically normal to the outside surface and proceed to the inside surface with less than 30° deviation. These pits would most likely penetrate the inner surface first, but would also be the hardest to find from random sections. In the field, these would be easier to find because the places would be where the pressurized fluid leaked. For that reason, while this type of test attempts to model some field conditions, it did not necessarily give a definitive measurement of pit depth.

Also noted, in a given cross-section the deepest formicary pit was randomly located over the circumference, including the weld.

One aspect of the fifty-day test was an occasional morphology where the copper tube section displayed thin blue lines. Generally, etching revealed instances of preferential intergranular attack at areas coincident with thin blue lines. (See photographs of Appendix C). These instances were observed of what appeared to be preferential grain attack. Therefore, it was postulated that there was a relation between intergranular attack and the direction changes characteristic of formicary corrosion. Notoya (1997a) reported occasional instances of this morphology from his laboratory studies and reported a single instance from field exposures. Even though Notoya (1997c) concluded that there was no relationship between formicary

corrosion and intergranular attack, based on his studies using copper of different grain sizes, it was concluded from this study that the cause of the random directional changes typical of formicary corrosion was attributed to intergranular corrosion.

4.3.3. Input Variable Influence

The influence of the input variables on the copper tubes has been assessed. A chart of pit depth versus temperature is shown to the left of the text for each acid concentration in the six-month test. As noted in the statistical report, interactions between some of the variables are a complicating factor.

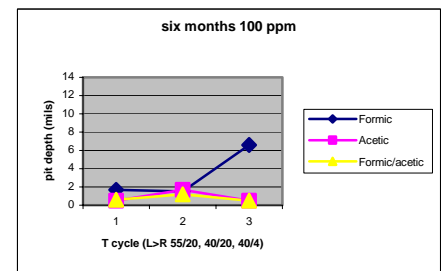
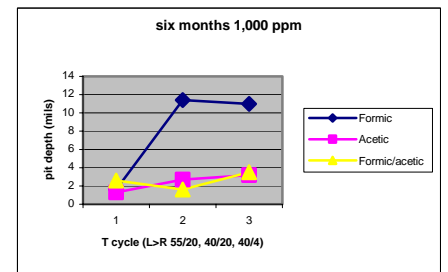
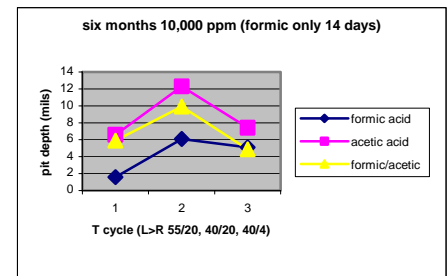
Acid concentration: Bearing in mind that the formic acid data in the 10,000-ppm chart is after 14-days, (all the other data is after 6-months), the 10,000-ppm concentration is clearly more aggressive than the 1,000-ppm concentration. The difference between the 1,000 and 100-ppm is also clear. As can be seen in the photographs in Appendix C, At 10,000-ppm the tubes were heavily encrusted with corrosion product after 6-months. At 1,000-ppm corrosion products were visible and the tubes were tarnished, at 100-ppm the tubes were less tarnished and corrosion products were more visible with the unaided eye on the formic acid tubes. The pit type seen in the formic acid was usually branching, although at the 50/20°C cycle the largest pits were circular or undeveloped branching. The acetic acid and formic/acetic mixture usually had circular pitting, but some branching was seen in both, especially the formic/acetic mixture. The branching in these two solutions was more noticeable at the lower concentrations.

Inverse proportion of acetic acid: on average the formic acid is much more aggressive than the acetic acid mixture, which is somewhat more aggressive than the formic/acetic.

The high temperature: A rule of thumb is that the rate of a chemical reaction doubles for each ten degree centigrade increase in temperature. This was not the case in these tests. At 10,000-ppm the 55/20°C cycle was significantly lower than the 40/20°C cycle in observed pit depth. This holds true for the formic at

1,000-ppm; but the other two solutions do not show temperature having much effect. At 100-ppm all three solutions are close at these two cycles.

The low temperature: This also varied by concentration and acid. At 10,000-ppm the formic showed a slight decline in pit depth from the 40/20°C cycle to the 40/4°C cycle, while the other two solutions showed a pronounced decline. At 1,000-ppm the formic acid again showed a slight decline, but the other two solutions showed a slight increase. At 100-ppm the formic acid showed a large increase, and the other two showed a slight decline.



Days: As discussed earlier, the 10,000-ppm solutions showed a strong correlation between pit depth and length of exposure and the 1,000-ppm solutions a slightly less strong correlation. The 100-ppm solutions had more variation, but this may be an indication that at lower concentrations the pit depth needs to be measured at more than three cross-sections. All of the tubes were bright and shiny when the test was started, but as the exposure period lengthened the tubes became increasingly tarnished and then corrosion products began building up on the outside surface. The 10,000-ppm concentration turned a dark brown within twenty-four hours. The 1000-ppm tubes had turned brown within a week, and all of the 100-ppm tubes except for the acetic and formic/ acetic at the 40/4°C cycle had turned brown within three weeks.

5. TEST METHOD FOR SCREENING FLUIDS

5.1. Procedures

Twelve (12) oil samples were submitted blindly, and screened using thermal degradation and hydrolysis.

5.1.1. Thermal degradation

Crushed alundum boiling chips (0.01 gram) were placed into a culture tube with one gram of test fluid. The culture tube was then placed into an oven (preheated to 200°C) for one hour. After cooling to room temperature the fluid was reweighed and analyzed using FTIR to determine if the sample had degraded to form carboxylic compounds. The remaining fluid in the culture tube was then reweighed and two grams of deionized water was added. The culture tube was covered with a piece of food grade polyethylene and vigorously shaken for 30-seconds before centrifuging for 30-seconds. The water phase was pipetted into a syringe fitted with a 0.45-micron filter and analyzed by IC for the presence of carboxylates [such as formate (formic acid) and acetate (acetic acid)].

5.1.2. Hydrolysis

One gram of crushed alundum boiling chips were combined with 90-grams of a submitted oil and ten grams of deionized water in a pressure vessel which was sealed and placed into an oven preheated to 100°C) for 48-hours. After cooling to room temperature the water phase was pipetted into a syringe fitted with a 0.45-micron filter and analyzed by IC for the presence of carboxylates.

5.2. Results

The results of the oil testing are shown in Table 9 of Appendix B.

5.3. Discussion

The quantities of carboxylic species found varied widely, reflecting the wide variety of fluids that were submitted blindly and tested. Some oils generated significant amounts of formate and/or acetate, while others were absent of these species. The hydrolysis method produced higher levels of both acids than thermal degradation did for six of the fluids. More data would be needed to determine probable trends or benefits for hydrolysis versus thermal degradation.

6. CONCLUSIONS

Based on the results of these studies, the following conclusions were made:

6.1. Formicary Testing

6.1.1 Formicary corrosion continues to baffle investigators who have yet been able to prove a mechanism, much less be able to predict behavior, except to acknowledge that it requires four elements to simultaneously occur, namely air (oxygen), moisture (water), a low molecular weight organic acid (possibly a decomposed fluid), and a copper alloy.

6.1.2. 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 the initiation and propagation of formicary corrosion.

6.1.3. 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 apparently random tunneling observed in cross-sections.

6.1.4. The critical concentration of formic acid needed to initiate formicary attack is less than 20- ppm.

6.1.5. Significant formicary corrosion may occur within ten days of exposure even at a low (20-ppm) concentration of formic acid.

6.1.6. The breakdown of ethylene glycol can lead to formicary corrosion.

6.1.7. The most important input variables to maximum pit depth (in descending order) are:

- log concentration of the acids
- the inverse proportion of acetic acid
- the high temperature (T-hi)
- the low temperature (T-low)
- the length of exposure (in days)

6.1.8. The five inputs variables accounted for 62% of the variance in the maximum depth. This number would increase if input interactions were considered.

6.1.9. Even under laboratory conditions formicary corrosion can behave unpredictably.

6.2. Fluid Analyses

6.2.1. The formicary corrosion tests have shown that formic acid concentrations as low as 20-ppm can result in formicary pitting as great as 2.1-mils deep within ten-days.

6.2.2. A critical value for formicary corrosion initiation has not been established however:

- Formicary corrosion can be expected when the hydrolyzed suspect fluid contains greater than 20-ppm of formic acid.
- Fluids with more than 20-ppm of formic acid warrant attention, and should not be utilized if formicary corrosion can impact product use.
- Fluids with less than 20-ppm of formic acid should be further evaluated by copper tube exposure testing and metallographic assessment.

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APPENDIX A
FORMICARY TESTING PROCEDURE

A. FORMICARY TEST PROCEDURE

A.1. Test Preparation

A.1.1. Copper Tube Preparation

Handle the copper tubes with clean gloves. The copper tubes are cut to the desired length (5-cm to 6.4-cm) with a dry diamond saw. Clean the saw blade with methanol and then acetone. Burrs are removed by using dry 600-grit paper. Internal burrs are removed by using the deburring tool (clean before use).

An identity number is engraved at the bottom of each tube and a small notch made on each end with a small triangular file serves to define the tube orientation throughout the test; the Gore-Tex™ string also fits into these notches. Rinse the copper tubes with methanol and acetone and warm air dry.

A.1.2. Jar Preparation

The preferred jars for formicary experiments are one-liter, glass canning jars with a wire bale, hinged lid, and rubber gasket, which is isolated from the test vapor with a thin film of polyethylene.

New jars are rinsed with dionized water three times and allowed to air dry. Used jars are cleaned with soap, hot water and a bottlebrush, rinsed until there is no evidence of soap bubbles, rinsed three more times with tap water, then rinsed three times with dionized water and air dried. The lids are cleaned in a similar manner.

A.1.3. Solution Preparation

A 1% (10,000-ppm) solution of the desired acid is prepared; the solution should then be tested using IC and the acid concentration adjusted accordingly. The 1% solution can then be diluted to make solutions of 1,000-ppm and 100-ppm formate respectively, samples of untested solutions should be retained in case further testing is warranted.

A.1.4. Assembly

Copper tube samples are threaded with lengths of Gore-Tex™ string and supported near the top of the jar with the identity number down and the tube at a 45-degree angle. The string is taped in position to the outside of the jar and the lid is loosely placed into position. 100-mL of the test solution is poured into the jar using a long neck funnel to insure no splash contact onto the tubes; the lid is tightly fastened. Each jar should be clearly labeled with test solution, concentration, date test started, and any other information.

A.2. Experimental

A.2.1. Test Procedure

Jars are placed in a air convection laboratory oven. Overnight, the oven operates isothermally at the selected temperature. For weekday mornings the oven is turned off and the door left ajar, unless the test requires the jars to be chilled, in which case they are placed in a suitable refrigerator at a pre-set low temperature.

Jars are carefully examined daily to look for evidence of significant changes including: copper tube darkening, formation of blue or green crystals or change in solution color. Daily inspections can be stopped once changes are not discernable, weekly monitoring is then sufficient.

A.2.2. Removal of the Copper Tube Segment

A copper tube is removed from the jar and the lid immediately retightened. A 6-mm to 9-mm section is cut from the top of the tube according to the procedure noted above; this section is placed in a small zip lock bag.

If the copper tube is to be further exposed, then it is notched in line with the remaining notch on the tube bottom, to maintain the same orientation of the tube in the test jar. The tube is then replaced in the jar and the lid retightened.

A.2.3. Visual and Metallographic Evaluation

Before mounting, the the copper section is examined visually and macroscopically to detail physical features or discolorations. The sections are too fragile to be mounted conventionally; they should be first vacuum impregnated with a clear epoxy and then prepared as lateral sections for microscopic examination.

The polished cross-sections are evaluated for depth of formicary corrosion and other types of pitting. Pitting density, (defined earlier) is determined based on the number of pits visible on 1/3 of the outside surface of a cross-section of the copper tube at 25x magnification.

A.3. EVALUATING FLUID SUSCEPTABILITY TO FORMICARY CORROSION

The basic procedure, developed as a result of the testing, involves analysis by FTIR and IC

A.3.1. FTIR

Suspect fluids are analyzed using FTIR in the as-received condition and after exposure to 200°C for 1 hour.

A.3.1.1. As-received

The as-received fluid is analyzed by FTIR straight from the stock.

A.3.1.2. Thermal Degradation

Alumina (0.01-g) [note: aluminum oxide can catalyze the decomposition of certain lubricants] is weighed in a culture tube and 1-g of the test fluid [recordis added immediately prior to capping with aluminum foil. The tube is then placed into an oven preheated to 200°C for 1-hour. Once cooled to room temperature the sample is reweighed and analyzed by FTIR.

A.3.2. HYDROLYSIS

Suspect fluids are mixed with deionized water under various conditions to determine if they can be hydrolyzed to form organic acids.

A.3.2.1. As-received

Water is mixed with the as-received fluid at room temperature and the water phase analyzed by IC for the presence of carboxylates [such as formate (formic acid) and acetate (acetic acid)].

1g of the test fluid is mixed with 2-g of deionized water in a culture tube, covered with food-grade, plastic wrap [polyethylene], and shaken vigorously for 30-seconds. The fluid is centrifuged for 30-seconds and the water phase pipetted into a syringe fitted with a 0.45-micron filter to collect the IC sample for analysis.

A.3.2.2. With Boiling Water

The as-received suspect fluid is mixed with deionized water and heated to 100°C for 48-hours. The water phase is analyzed by IC for the presence of carboxylates [such as formate (formic acid) and acetate (acetic acid)].

Alumina (1-g) is added to 90-g of the suspect fluid and 10-g of deionized water in a pressure bottle which is sealed and placed into an oven preheated to 100°C for 48-hours. After cooling to room temperature the water phase is pipetted into a syringe fitted with a 0.45-micron filter to collect the IC sample for and analysis.

A.3.2.3. Thermally Degraded

An additional water extraction is made of the thermally degraded test fluid from the FTIR analysis (section A.2.1b), 2g of deionized water is added to the fluid in a culture tube, covered with food-grade, plastic wrap [polyethylene] which is shaken vigorously for 30 seconds and centrifuged for 30 seconds. The water phase is pipetted into a syringe fitted with a 0.45 micron filter to collect IC sample for analysis.

A.4. RESULTS

A.4.1. FTIR

The fluid analysis will indicate if there is a significant presence of a carbonyl (C=O) group (between wavenumbers 1600 and 1750) in the as-received condition and after thermal degradation. If there is a positive presence of a carbonyl, then these fluids have the potential of forming carboxylic acids (i.e., formic and/or acetic acid) that are known to cause formicary corrosion.

A.4.2. IC

The analytical results will be calculated as if all of the carboxylates are from the original mass of the test fluid as ppm, parts per million.

APPENDIX B
TABLES OF TEST RESULTS

Table 1
Six-Month Testing Formicary Summary

Solution	ppm	°C/°C max/min	Max Formicary Depth (mils)					
			Pre 70 ¹ - Days		70-Days	182-Days		
			Day	Max	Max	Max		
Formic Acetic 0.20 Formic 0.80 Acetic	10,000	55/20	14	1.6				
		40/20	14	6.1				
		40/4	14	5.9				
		Acetic	10,000	55/20	16	1.0	2.0	6.6
				40/20	16	3.0	4.5	12.1
				40/4	16	1.0	3.5	7.4
		0.20 Formic 0.80 Acetic	10,000	55/20	14	0.9	3.5	5.9
				40/20	16	4.3	6.9	9.9
				40/4	16	2.2	3.9	4.9
Formic Acetic 0.20 Formic 0.80 Acetic	1,000	55/20	35	0.4	1.2	1.6		
		40/20	49	10.2	11.8	11.4		
		40/4	51	6.3	7.3	11.0		
		Acetic	1,000	55/20	51	0.8	1.7	1.3
				40/20	50	2.0	3.5	2.7
				40/4	51	1.2	2.0	3.2
		0.20 Formic 0.80 Acetic	1,000	55/20	51	2.4	1.4	2.6
				40/20	50	1.3	1.4	1.6
				40/4	51	3.4	2.8	3.5
Formic Acetic 0.20 Formic 0.80 Acetic	100	55/20	51	1.7	1.2	1.7		
		40/20	50	2.4	3.0	1.5		
		40/4	51	5.5	5.1	6.6		
		Acetic	100	55/20	51	0.5	0.5	0.5
				40/20	51	0.9	0.8	1.7
				40/4	51	0.2	0.4	0.5
		0.20 Formic 0.80 Acetic	100	55/20	51	0.6	1.4	0.6
				40/20	51	0.6	0.5	1.2
				40/4	51	0.2	0.2	0.5
Ethylene glycol extract #1 Thermal degraded	Corroded Al added	55/20	52	0.1	0.4	0.3		
		40/20	52	0.2	0.3	0.6		
		40/4	52	0.2	0.2	0.7		
Ethylene glycol extract #2 hydrolysis	Corroded Al added	55/20	52	-	-	-		
		40/20	52	0.1	0.2	0.2		
		40/4	52	0.1	0.1	-		
	Uncorroded Al added	100	55/20	52	0.2	0.2	-	
			40/20	52	0.1	0.1	0.1	
			40/4	52	-	0.1	-	

- means no pits were observed

¹The pre 70-day data is from only 1 polishing location; those from 70 and 182-days are the deepest of 3-locations.

Table 2
Day 14-52 Evaluations

Solution	ppm	°C/°C max/min	Days On Test	Regular ¹ pitting (mils)		Formicary pitting (mils)		OutsidePitting Density 25x ²
				Max	Avg ³	Max	Avg	
Formic	10,000	55/20	14	2.2	2.2	1.6	0.9	21
		40/20	14	5.9	2.9	6.1	5.3	29
		40/4	14	3.0	2.6	5.9	4.5	21
Acetic		55/20	16	3.0	2.2	1.0	1.0	42
		40/20	16	2.6	2.0	3.0	1.7	26
		40/4	16	1.2	1.0	1.0	0.8	13
0.20 Formic 0.80 Acetic		55/20	14	1.3	0.7	0.9	0.7	11
		40/20	16	1.2	1.0	4.3	3.2	11
		40/4	16	1.6	1.0	2.2	2.0	6
Formic	1,000	55/20	35	0.2	0.2	0.4	0.2	0
		40/20	49	0.6	0.4	10.2	8.7	27
		40/4	51	0.6	0.4	6.3	5.4	13
Acetic		55/20	51	0.5	0.2	0.8	0.4	6
		40/20	50	0.4	0.2	2.0	1.3	24
		40/4	51	0.2	0.2	1.2	0.7	0
0.20 Formic 0.80 Acetic		55/20	51	0.6	0.5	2.4	1.4	5
		40/20	50	0.5	0.3	1.3	0.8	30
		40/4	51	0.2	0.2	3.4	1.9	0
Formic	100	55/20	51	0.2	0.2	1.7	1.3	5
		40/20	50	0.4	0.2	2.4	1.8	4
		40/4	51	0.6	0.4	5.5	4.6	6
Acetic		55/20	51	0.4	0.3	0.5	0.3	1
		40/20	51	0.8	0.5	0.9	0.8	16
		40/4	51	0.3	0.3	0.2	0.2	0
0.20 Formic 0.80 Acetic		55/20	51	0.1	0.1	0.6	0.4	0
		40/20	51	0.2	0.2	0.6	0.4	3
		40/4	51	0.2	0.1	0.2	0.1	0
Ethylene glycol extract #1 Thermal degraded	Corroded Al added	55/20	52	0.1	0.1	0.1	0.1	0
		40/20	52	0.1	0.1	0.2	0.1	0
		40/4	52	0.2	0.2	0.2	0.2	0
Ethylene glycol Extract #2 hydrolysis	Corroded Al added	55/20	52	-	-	-	-	0
		40/20	52	0.1	0.1	0.1	0.1	0
		40/4	52	0.1	0.1	0.1	0.1	0
	Uncorroded Al added	55/20	52	0.1	0.1	0.2	0.2	0
		40/20	52	-	-	0.1	0.1	0
		40/4	52	-	-	0.1	0.1	0

- means none observed

¹Regular pitting is pitting with neither branching nor deposits with a blue color.

² Pitting density is the number of pits observed on 1/3 of the outer circumference of a cross-section at 25x magnification

³ Avg is the average of the 5 deepest pits. If there are fewer than 5 pits observed, it is the average of the observed pits.

Table 3
Day Seventy Evaluations

Solution.	ppm	°C/°C max/ min	Formicary pitting (mils) Location ¹						Outside Pitting ² Density 25x Location		
			1		2		3		1	2	3
			Max	Avg ³	Max	Avg	Max	Avg			
Acetic	10,000	55/20	2.0	1.7	2.0	1.4	1.2	1.0	19	14	19
		40/20	4.1	4.0	4.5	2.8	3.5	3.0	30	16	12
		40/4	3.3	2.5	3.2	2.6	3.5	2.6	20	10	6
0.20 Formic 0.80 Acetic		55/20	3.5	2.6	2.6	1.4	3.0	1.7	20	7	14
		40/20	6.9	3.7	3.3	2.5	5.3	3.4	12	10	16
		40/4	3.0	2.8	3.9	2.4	3.0	1.7	9	11	15
Formic	1,000	55/20	1.0	0.8	1.0	0.8	1.2	0.9	4	4	5
		40/20	6.5	6.1	11.8	10.6	11.0	8.7	15	16	18
		40/4	5.3	4.1	6.7	5.4	7.3	5.1	9	14	12
Acetic		55/20	1.6	1.1	1.6	1.1	1.7	1.1	1	5	16
		40/20	3.5	1.8	2.2	1.6	1.8	1.2	10	10	16
		40/4	0.8	0.7	2.0	1.2	1.2	0.9	5	4	7
0.20 Formic 0.80 Acetic	55/20	1.4	0.9	1.2	1.0	0.8	0.6	8	3	5	
	40/20	1.4	1.0	1.2	0.9	1.0	0.8	7	6	7	
	40/4	1.8	1.5	2.6	2.0	2.8	2.2	1	3	5	
Formic	100	55/20	0.8	0.7	0.7	0.6	1.2	0.7	1	4	6
		40/20	1.6	1.0	2.0	1.2	3.0	1.1	2	3	5
		40/4	5.1	3.5	3.5	2.3	3.3	2.7	9	10	22
Acetic		55/20	0.5	0.4	0.5	0.3	0.5	0.3	0	2	0
		40/20	0.7	0.6	0.8	0.6	0.8	0.5	5	6	2
		40/4	0.2	0.2	0.3	0.2	0.4	0.2	0	1	1
0.20 Formic 0.80 Acetic	55/20	1.4	0.5	0.2	0.1	0.2	0.1	1	0	0	
	40/20	0.4	0.3	0.5	0.3	0.4	0.2	0	1	0	
	40/4	0.4	0.2	0.2	0.2	0.2	0.1	0	0	0	
Ethylene glycol extract #1 Thermal degraded	Corroded Al added	55/20	0.1	0.1	0.4	0.4	0.2	0.1	0	0	0
		40/20	0.2	0.2	0.3	0.2	-	-	0	0	0
		40/4	0.2	0.1	-	-	0.2	0.1	0	0	0
Ethylene glycol extract #2 hydrolysis	Corroded Al added	55/20	-	-	-	-	-	-	0	0	0
		40/20	0.1	0.1	-	-	0.2	0.1	0	0	0
		40/4	0.1	0.1	-	-	-	-	0	0	0
	Uncorroded Al added	55/20	0.2	0.2	-	-	-	-	0	0	0
		40/20	0.1	0.1	-	-	-	-	0	0	0
		40/4	0.1	0.1	-	-	0.1	0.1	0	0	0

- means none observed

¹ Each mount was ground to and evaluated at three depths, e.g. "location" 1, 2 and 3.

² Pitting density is the number of pits observed on 1/3 of the outer circumference of a cross-section at 25x magnification.

³ Avg is the average of the 5 deepest pits. If there are fewer than 5 pits observed, it is the average of the observed pits.

Table 4
Six-Month Evaluations (Acids)

Solution	ppm	Where on tube the section was cut	°C/°C max/min	Formicary pitting (mils) Location ¹						Outside Pitting Density ² 25x Location					
				1		2		3		1		2		3	
				Max	Avg	Max	Avg ⁴	Max	Avg	#	Branch ratio ³	#	Branch ratio	#	Branch ratio
Acetic	10,000	Top	55/20	5.8	5.0	5.4	5.2	6.6	5.7	13	0/13	7	0/7	10	0/10
		Top	40/20	12.3	11.8	11.5	11.2	12.1	10.8	16	0/16	17	0/17	9	0/9
		Top	40/4	4.8	4.3	4.8	4.1	7.4	5.5	12	0/12	9	0/9	8	0/8
		Top	55/20	3.2	2.7	5.5	4.3	5.9	4.1	27	0/27	19	0/19	15	0/15
		Top	40/20	9.9	9.2	8.8	6.6	8.2	7.6	13	1/13	10	0/10	28	0/28
		Top	40/4	4.8	4.0	4.9	3.8	3.3	3.0	16	2/16	15	0/15	43	6/43
Formic	1,000	Top	55/20	1.6	1.3	0.9	0.8	1.0	0.9	13	6/13	25	13/25	30	10/30
		Top	40/20	10.6	7.1	8.5	6.8	11.4	7.7	16	11/16	20	11/20	30	17/30
		Top	40/4	7.1	6.5	10.0	7.5	11.0	8.2	23	18/23	28	19/28	28	22/28
		Mid		5.3	4.1					14	13/14				
		Bot		3.0	2.3					10	6/10				
Acetic		Top	55/20	0.9	0.8	0.6	0.6	1.3	0.7	2	0/2	4	0/4	3	0/3
		Top	40/20	2.7	2.3	2.5	1.5	1.6	1.4	4	0/4	10	2/10	15	3/15
		Top	40/4	3.2	1.7	1.7	1.4	2.1	1.5	5	0/5	14	2/14	24	3/24
		Mid		1.2	1.1					15	0/15				
		Bot		1.1	1.1					8	0/8				
0.20Formic / 0.80Acetic		Top	55/20	2.5	1.6	2.6	1.5	1.4	1.2	10	1/10	12	2/12	9	2/9
		Top	40/20	1.6	1.3	1.5	1.2	1.4	1.3	75	1/75	48	0/48	43	2/43
		Top	40/4	3.5	2.6	2.1	1.4	1.8	1.4	51	2/49	36	2/36	29	2/29
Formic	100	Top	55/20	1.3	0.9	1.2	1.0	1.7	1.4	13	2/13	19	4/19	7	3/7
		Top	40/20	1.3	0.9	1.5	1.0	1.3	1.0	4	1/4	3	2/3	9	5/9
		Top	40/4	6.6	4.8	5.5	4.6	4.7	3.7	24	13/24	33	11/33	39	26/39
		Bot		4.1	1.6					3	0/3				
Acetic		Top	55/20	0.4	0.4	0.4	0.3	0.5	0.3	1	0/1	0		1	0/1
		Top	40/20	1.7	1.2	1.5	1.0	1.7	1.2	6	2/6	5	0/5	17	2/17
		Top	40/4	0.4	0.3	0.5	0.4	0.4	0.3	1	0/1	2	1/2	1	0/1
		Mid		0.5	0.2					0					
		Bot		0.6	0.3					1	0/1				
0.20Formic / 0.80Acetic		Top	55/20	0.6	0.4	0.3	0.3	0.4	0.4	1	0/1	0		0	
		Top	40/20	1.2	0.8	0.9	0.7	0.4	0.3	11	1/11	4	1/4	0	
		Top	40/4	0.4	0.3	0.5	0.3	0.3	0.2	5	0/5	1	1/1	0	
		Mid		0.3	0.2					1	1/1				

¹ Each mount was ground to and evaluated at three depths, e.g. "location" 1, 2 and 3.

² Pitting density is the number of pits observed on 1/3 of the outer circumference of a cross-section at 25X magnification. This number is in the first column.

³ The 2nd column (Branch ratio) is the # of pits in the the pitting density with a branching morphology. If the pitting density was zero, the ratio is left blank.

⁴ Avg is the average of the 5 deepest pits. If there are fewer than 5 pits observed, it is the average of the observed pits.

Table 5
Six Month Evaluations (Deionized Water and Ethylene Glycols)

Solution		Where on tube the section was cut	°C/°C max/min	Regular pitting ³ (mils) Location ¹						Formicary pitting (mils) Location						Outside Pitting Density ² 25x Location		
				1		2		3		1		2		3		1	2	3
				Max	Avg ⁴	Max	Avg	Max	Avg	Max	Avg	Max	Avg	Max	Avg			
Deionized water		Top	55/20	-	-	-	-	0.2	0.1	-	-	-	-	-	-	0	0	0
		Top	40/20	-	-	0.2	0.1	0.1	0.1	-	-	-	-	-	-	0	0	0
		Top	40/4	-	-	0.1	0.1	0.2	0.2	-	-	-	-	-	-	0	0	0
		Mid		0.1	0.1							-	-			0		
		Bot		0.1	0.1							-	-			0		
Ethylene glycol extract #1 Thermal degraded	Corroded Al added	Top	55/20	0.2	0.1	0.2	0.2	0.2	0.1	0.2	0.2	0.3	0.2	0.2	0.2	0	3	0
		Top	40/20	0.2	0.1	0.2	0.2	0.2	0.1	0.2	0.2	0.3	0.2	0.2	0.2	0	3	0
		Top	40/4	-	-	-	-	0.2	0.1	0.7	0.5	0.6	0.4	0.7	0.5	1	1	3
Ethylene glycol extract #2 hydrolysis	Corroded Al added	Top	55/20	0.3	0.2	0.1	0.1	-	-	-	-	-	-	-	-	0	0	0
		Top	40/20	0.2	0.2	0.2	0.1	0.2	0.1	0.2	0.1	0.1	0.1	-	-	0	0	0
		Top	40/4	0.2	0.2	-	-	-	-	-	-	-	-	-	-	0	0	0
	Uncorroded Al added	Top	55/20	0.1	0.1	0.2	0.1	-	-	-	-	-	-	-	-	0	0	0
		Top	40/20	-	-	-	-	-	-	0.1	0.1	-	-	-	-	0	0	0
		Top	40/4	-	-	-	-	-	-	-	-	-	-	-	-	0	0	0

- means none observed

¹ Each mount was ground to and evaluated at three depths, e.g. “location” 1, 2 and 3.

² Pitting density is the number of pits observed on 1/3 of the outer circumference of a cross-section at 25X magnification. This number is in the first column.

³ Regular pitting is non formicary, e.g. with neither a branching morphology nor blue colored deposits.

⁴ Avg is the average of the 5 deepest pits. If there are fewer than 5 pits observed, it is the average of the observed pits.

Table 6
50 Day Test Evaluations (40°/20°C cycle)

Days	Tube#	Formic Acid ppm	Formicary pitting (mils)						Outside Pitting Density 25x ²						Summary (maxima)		
			Location ¹						Location						Pit Depth (mils)	Avg Depth (mils)	Pit Density
			1		2		3		1		2		3				
Max	Avg ⁴	Max	Avg	Max	Avg	#	Branch ³ ratio	#	Branch ratio	#	Branch ratio						
10	1	100	0.7	0.5	1.2	0.9	1.0	0.8	2	1/2	1	1/1	3	3/3	1.2	0.9	3
	2		4.0	1.7	6.1	2.4	3.6	1.9	5	5/5	4	4/4	4	4/4	6.1	2.4	5
	3	50	0.9	0.7	0.6	0.4	2.1	0.9	3	3/3	0		1	1/1	2.1	0.9	3
	4		0.7	0.3	0.7	0.3	0.5	0.4	1	1/1	0		0		0.7	0.4	1
	5	20	0.8	0.5	1.2	0.8	0.9	0.7	2	1/2	1	1/1	4	4/4	1.2	0.8	4
	6		1.2	0.7	2.1	0.7	0.9	0.5	1	1/1	1	1/1	1	1/1	2.1	0.7	1
20	7	100	0.5	0.3	0.5	0.3	0.4	0.3	1	1/1	0		0		0.5	0.3	1
	8		0.8	0.7	1.4	1.1	0.9	0.8	2	2/2	2	2/2	1	1/1	1.4	1.1	2
	9	50	1.3	0.9	1.2	0.9	1.1	0.8	2	2/2	1	1/1	1	1/1	1.3	0.9	2
	10		1.7	0.8	2.8	1.7	3.6	2.3	2	2/2	4	4/4	6	6/6	3.6	2.3	6
	11	20	0.5	0.4	0.2	0.2	0.3	0.3	1	1/1	0		0		0.5	0.4	1
	12		0.2	0.2	0.2	0.2	0.3	0.1	0		0		0		0.3	0.2	0
30	13	100	2.4	1.5	1.7	1.4	0.8	0.6	5	5/5	5	5/5	1	1/1	2.4	1.5	5
	14		2.8	2.2	2.4	1.7	3.4	2.7	8	8/8	7	7/7	9	9/9	3.4	2.7	9
	15	50	4.7	2.6	5.8	3.9	2.7	2.4	6	6/6	13	13/13	7	7/7	5.8	3.9	13
	16		3.2	1.9	5.5	2.8	2.1	1.4	6	6/6	11	11/11	6	6/6	5.5	2.8	11
	17	20	2.9	1.8	2.1	1.6	2.1	1.7	3	3/3	4	4/4	5	5/5	2.9	1.8	5
	18		0.9	0.6	0.6	0.4	0.7	0.4	1	1/1	1	0/1	2	2/2	0.9	0.6	2
40	19	100	6.4	4.0	3.6	2.4	4.7	3.4	9	9/9	4	4/4	4	4/4	6.4	4.0	9
	20		1.7	1.3	3.3	2.4	3.4	2.3	4	4/4	4	4/4	6	6/6	3.4	2.4	6
	21	50	5.1	4.2	3.6	2.6	1.8	1.0	9	9/9	7	7/7	4	4/4	5.1	4.2	9
	22		3.0	1.7	3.2	1.5	1.9	1.0	2	2/2	2	2/2	1	1/1	3.2	1.7	2
	23	20	0.6	0.6	0.6	0.5	1.6	1.0	0		1	1/1	2	2/2	1.6	1.0	2
	24		1.4	0.8	1.4	1.1	1.8	1.0	3	3/3	2	2/2	1	1/1	1.8	1.1	3
50	25	100	5.2	4.4	7.1	4.4	5.1	2.9	6	6/6	6	6/6	5	5/5	7.1	4.4	5
	26		4.7	3.5	6.0	3.5	4.5	3.1	10	10/10	10	10/10	6	6/6	6.0	3.5	10
	27	50	5.1	4.6	6.0	4.2	4.6	3.3	14	14/14	13	13/13	11	11/11	6.0	4.6	14
	28		4.2	3.5	2.9	2.1	3.6	2.9	21	21/21	6	6/6	7	7/7	4.2	3.5	21
	29	20	1.9	1.4	2.7	2.2	1.7	1.3	5	4/5	6	6/6	9	9/9	2.7	2.2	9
	30		1.0	0.5	0.6	0.5	0.9	0.5	1	1/1	1	1/1	1	1/1	1.0	0.5	1

¹ Each mount was ground to and evaluated at three depths, e.g. "location" 1, 2 and 3.

² Pitting density is the number of pits observed on 1/3 of the outer circumference of a cross-section at 25X magnification. This number is in the first column.

³ The 2nd column (Branch ratio) is the # of pits in the the pitting density with a branching morphology. If the pitting density was zero, the ratio is left blank.

⁴ Avg is the average of the 5 deepest pits. If there are fewer than 5 pits observed, it is the average of the observed pits

Table 7
50-Day Test Summary
Maximum pit depths of 3 polishes (mils) 40/20°C cycle

Concentration (ppm)	Jar (A or B)	10 Days	20 Days	30 Days	40 Days	50 Days
100	A	1.2	0.5	2.4	6.4	7.1
100	B	6.1	1.4	3.4	3.4	6.0
50	A	2.1	1.3	5.8	5.1	6.0
50	B	0.7	3.6	5.5	3.2	4.2
20	A	1.2	0.5	2.9	1.6	2.7
20	B	2.1	0.3	0.9	1.8	1.0

Note: The A and B jars are duplicates. Identification as “A” or “B” is random

Table 8
Ion Chromatograph Testing of Six-Month Day Solutions

Solution	Type		Formic Acid (ppm)	Acetic Acid (ppm)	Ratio Formic:Acetic
Formic Acid	10,000 ppm	original	9536	-	-
		1,000 ppm	original	974	-
	1,000 ppm	55/20	584	-	-
		40/20	452	-	-
		40/4	516	-	-
	100 ppm	original	92.4	-	-
		55/20	78.4	-	-
		40/20	39.2	-	-
		40/4	60.4	-	-
	Ethylene Glycol		As purchased	1.2	1.3
Extract #1		original	8.0		
		55/20	33.3	386.4	1 : 11.6
		40/20	15.0	80.7	1 : 5.4
		40/4	17.4	114.0	1 : 6.6
Extract #2 w/ corroded Al added		original	17.8	14.2	1 : 0.8
		55/20	23.2	311.0	1 : 13.4
		40/20	17.5	166.1	1 : 9.5
		40/4	19.8	287.9	1 : 14.5
Extract #2 w/ uncorroded Al added		original	8.1	33.6	1 : 4.1
		55/20	17.3	305.9	1 : 17.7
		40/20	9.3	117.8	1 : 12.7
		40/4	11.2	146.3	1 : 13.1

The formic acid originals are retains that were tested after the end of the exposure test.

The ethylene glycol numbers have been adjusted for dilution, the mass of water added for extraction is back calculated out.

The IC determines formates and acetates, which equates to formic and acetic acids.

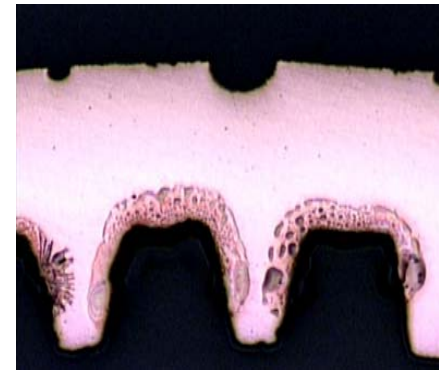
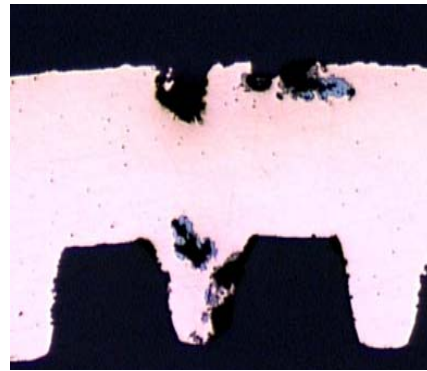
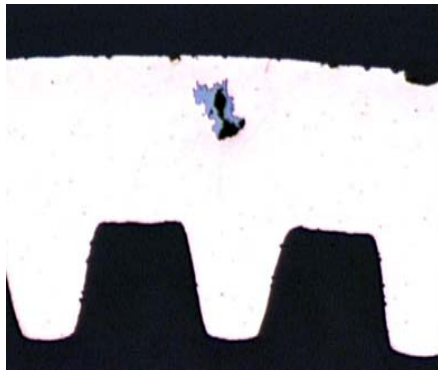
Table 9
Ion Chromatography Testing of Blindly Submitted Oils

Oil Reference Number	Method of Oil Degradation			
	Thermal Degradation		Boiling Water Hydrolysis	
	Acetate (ppm)	Formate (ppm)	Acetate (ppm)	Formate (ppm)
18082-1	0.3	0.7	2.4	6.6
18082-2	5.2	2.1	43	18
18082-3	3.6	3.1	10	39
18082-4	21	5.0	0	0
18082-5	16	9.2	61	18
18082-6	1.5	0	0.4	1.0
18082-7	729	406	580	160
18082-8	54	34	6.0	63
18082-9	1.8	0	0	0
18082-10	26	1.8	26	24
18082-11	3.0	3.0	6.6	9.1
18082-12	2.3	4.5	23	24

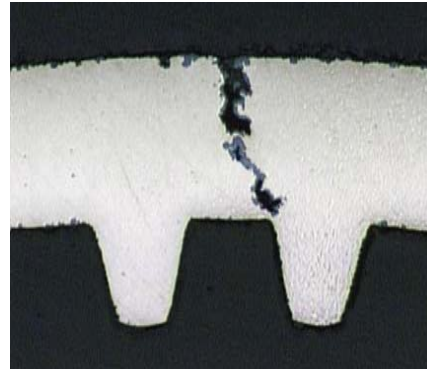
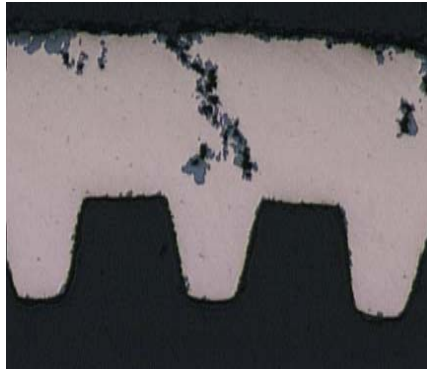
APPENDIX C
PHOTOGRAPHS OF CORROSION TESTING

Formic Acid Six-Month Exposure
(originals @125X magnification), (10,000-ppm only 14-day exposure)

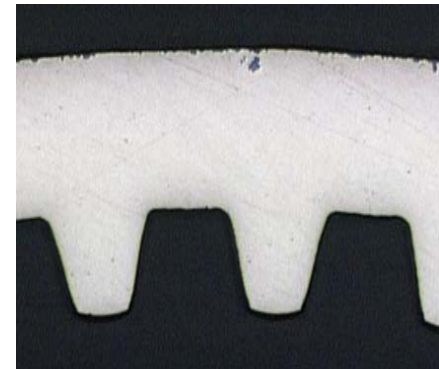
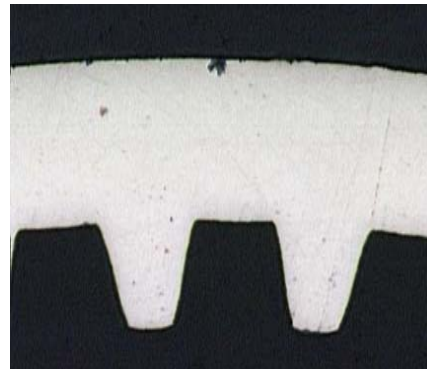
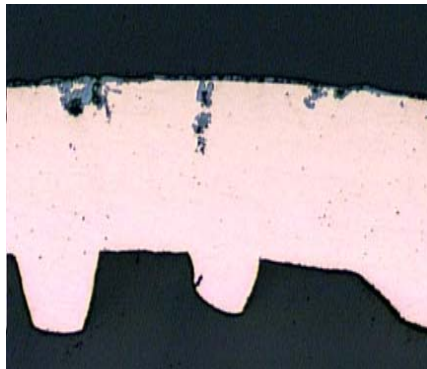
10,000-ppm



1,000-ppm



100-ppm



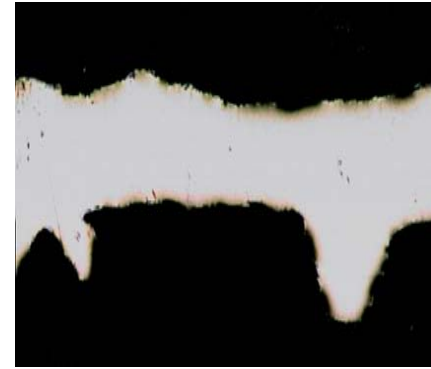
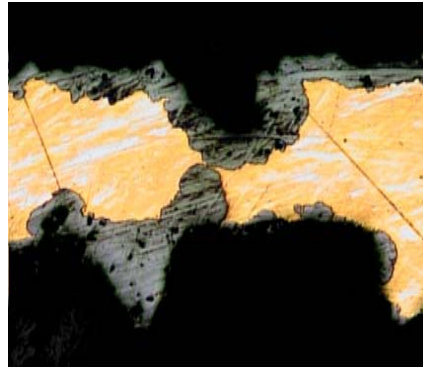
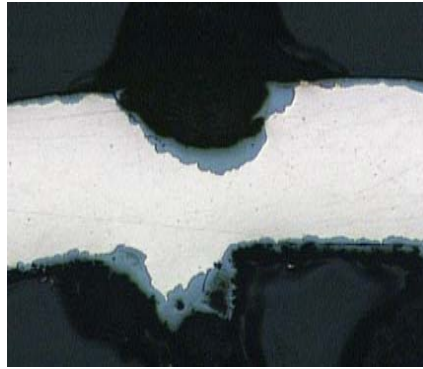
40/4°C

40/20°C

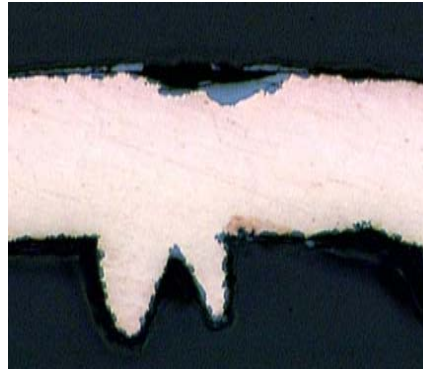
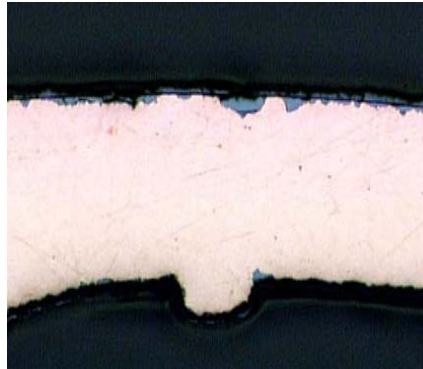
55/20°C

Acetic Acid Six-Month Exposure
(originals @125X magnification)

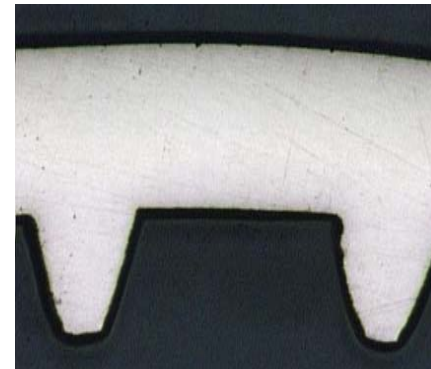
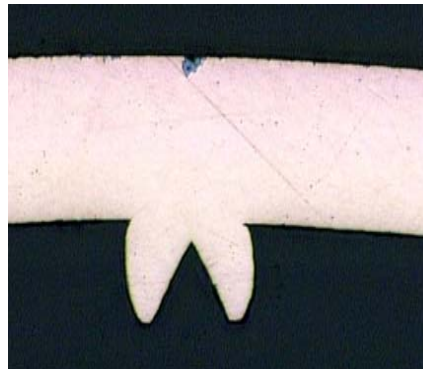
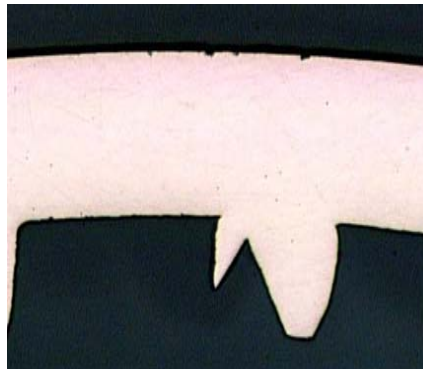
10,000-ppm



1,000-ppm



100-ppm



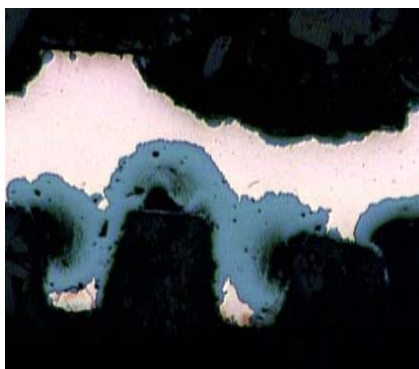
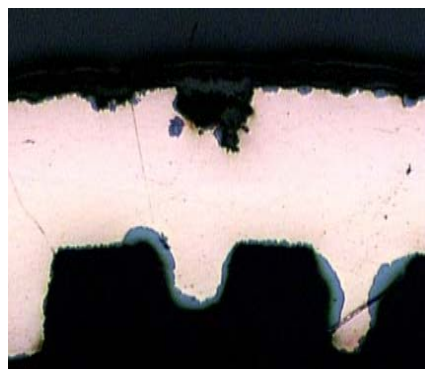
40/4°C

40/20°C

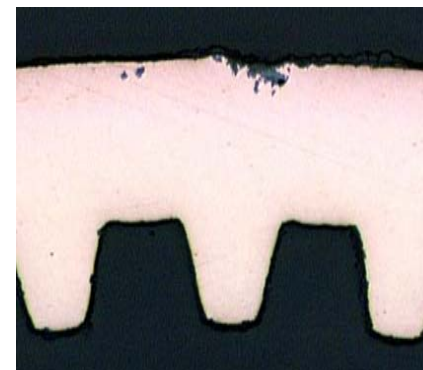
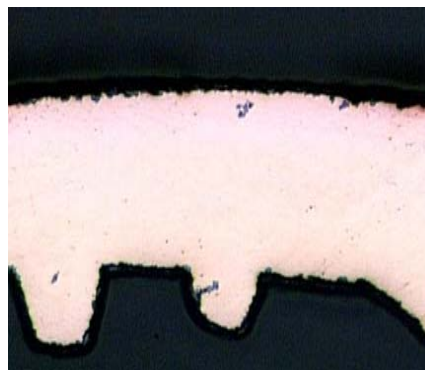
55/20°C

Formic Acid (20%) and Acetic Acid (80%) Six-Month Exposure
(originals @125X magnification)

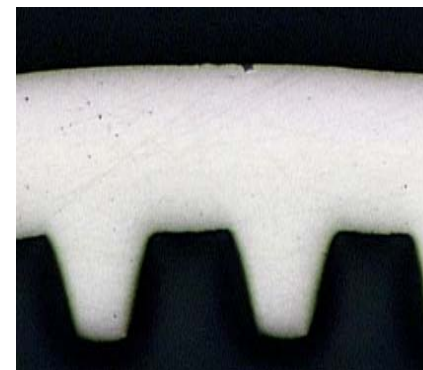
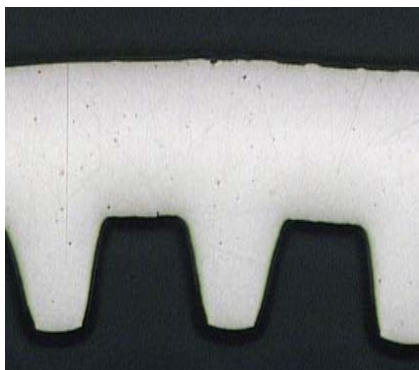
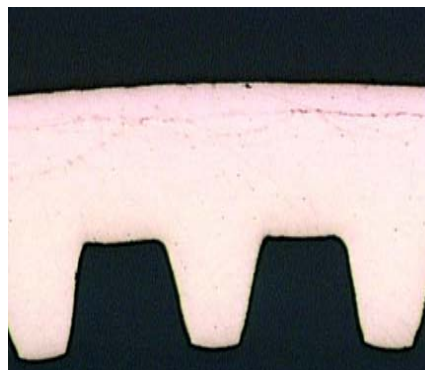
10,000-ppm



1,000-ppm



100-ppm



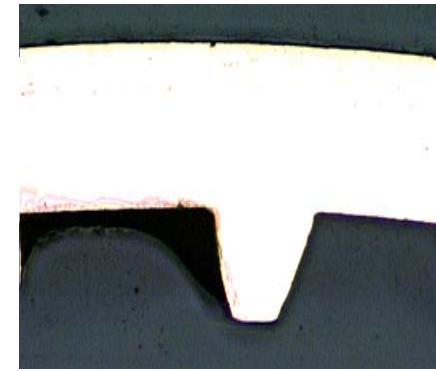
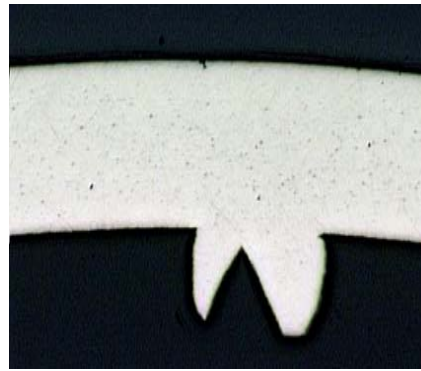
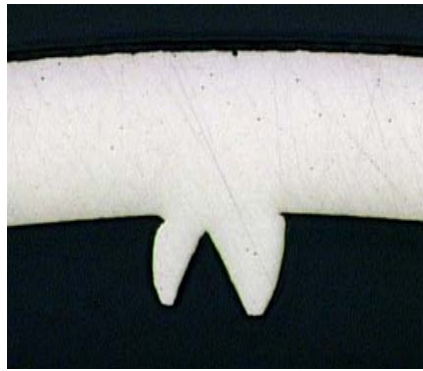
40/4°C

40/20°C

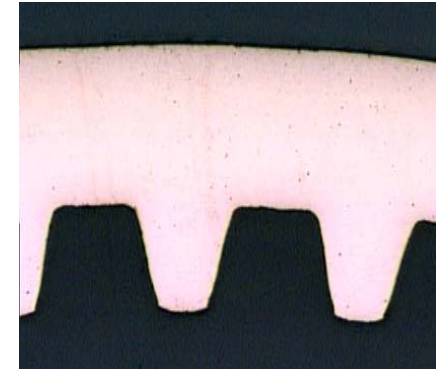
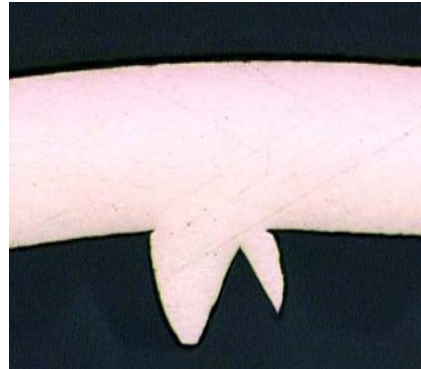
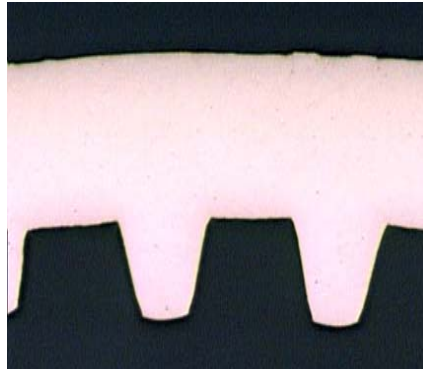
55/20°C

Ethylene Glycols at Six-Month Exposure
(originals @125X magnification)

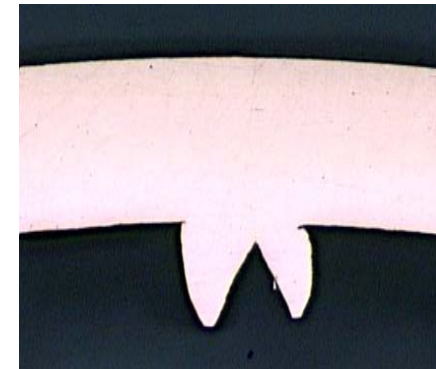
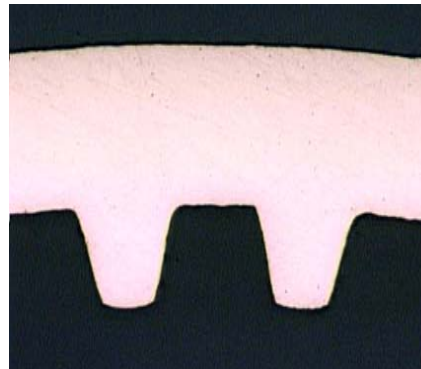
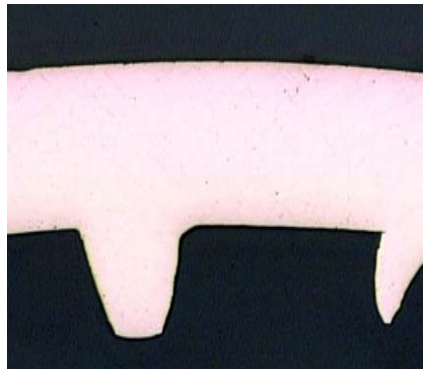
Extract #1
Thermally
Degraded



Extract #2
Hydrolysis
with
Corroded
Aluminum



Extract #2
Hydrolysis
with
un-corroded
Aluminum



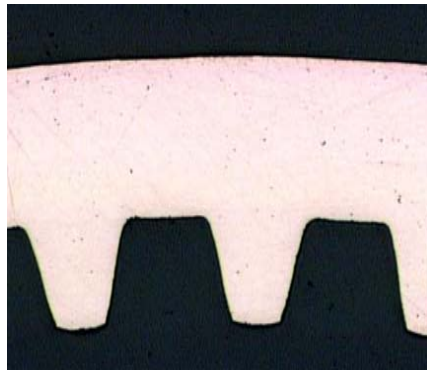
40/4°C

40/20°C

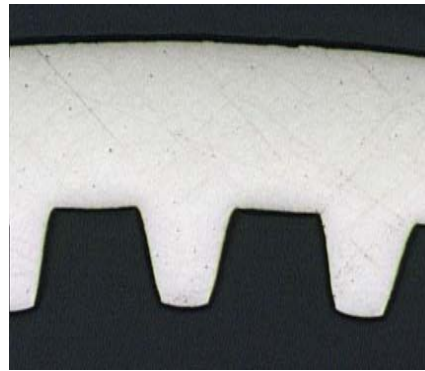
55/20°C

Deionized Water at Six Month Exposure
(originals @125X magnification)

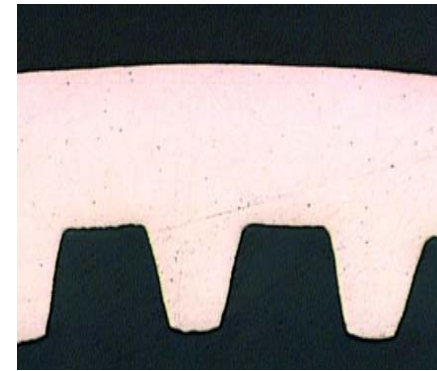
Deionized
Water



40/4°C



40/20°C



55/20°C

Typical Test Setup, six month test



Typical untested tube, approximately 2X



Tubes After Six-Month Exposure
(Approximately life-size, 10,000-ppm formic acid after 14-days exposure)

Formic Acid

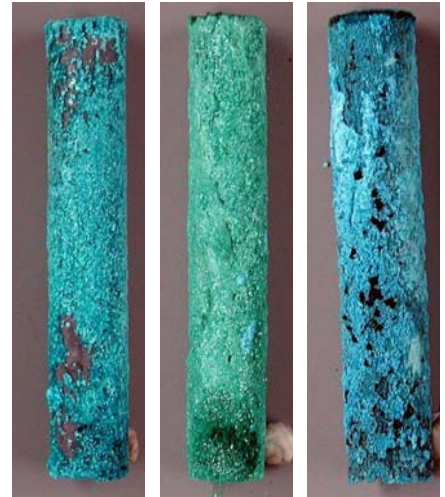
40/4°C 40/20°C 55/20°C

Acetic Acid

40/4°C 40/20°C 55/20°C

10,000-ppm

10,000-ppm



1,000-ppm

1,000-ppm



100-ppm

100-ppm



Tubes After Six Month Days Exposure
(Approximately life-size)

Formic Acid (20%)
Acetic Acid (80%)

Ethylene Glycol

40/4°C 40/20°C 55/20°C

40/4°C 40/20°C 55/20°C

10,000-ppm



Extract #1



1,000-ppm



Extract #2
with
corroded
aluminum
added



100-ppm



Extract #2
with
uncorroded
aluminum
added



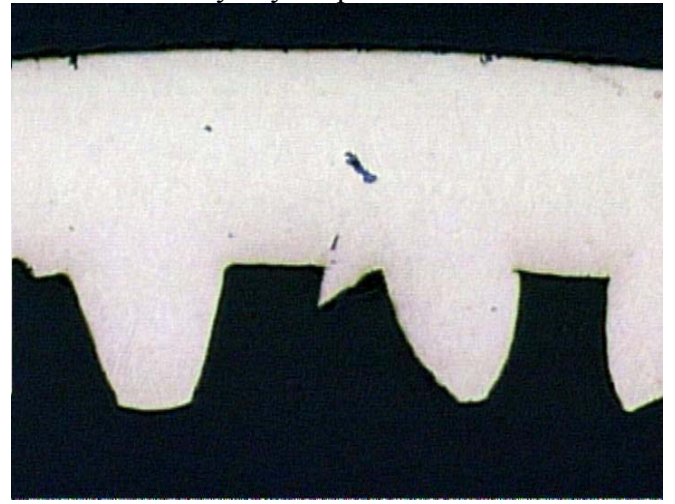
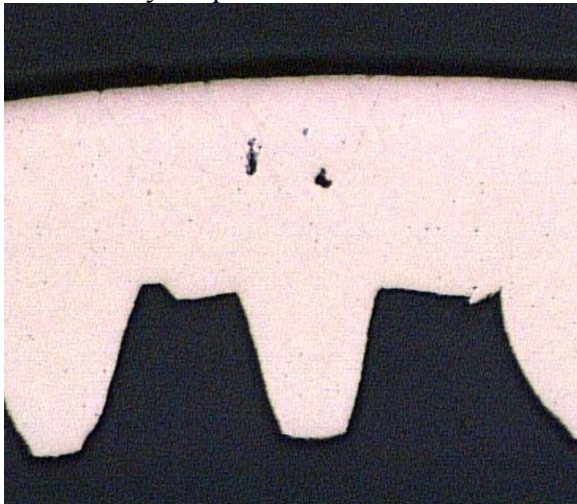
50-Day Formic Acid Test

40/20°C temperature cycle (originals @125x magnification)

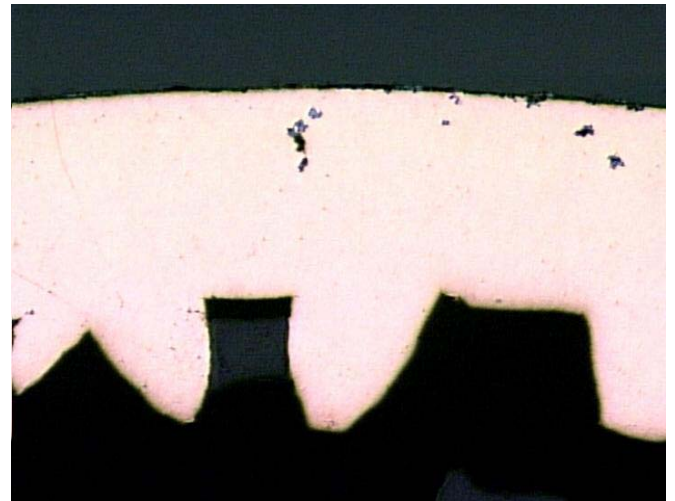
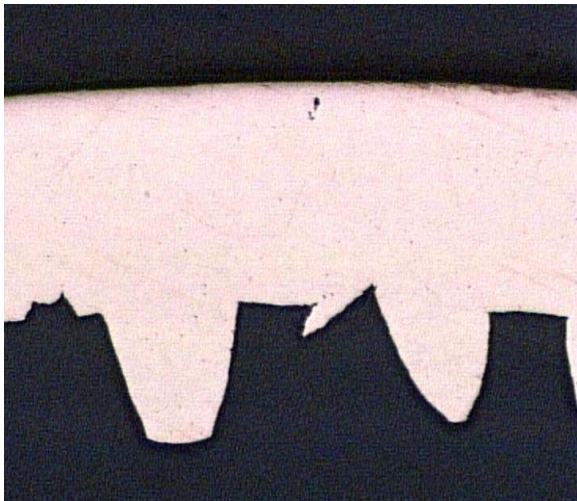
Ten days exposure

Fifty days exposure

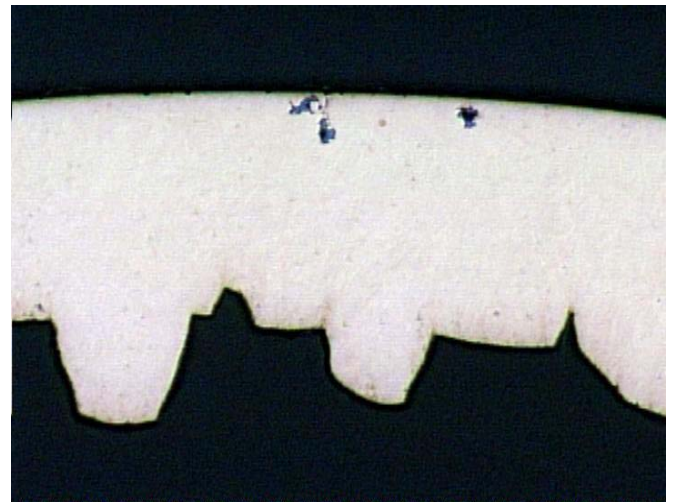
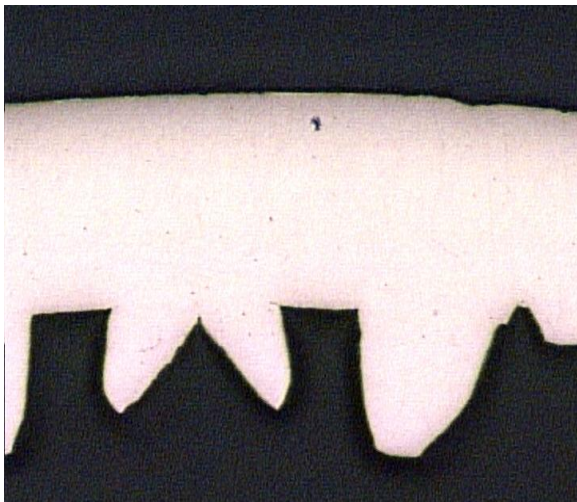
100-ppm









50-ppm



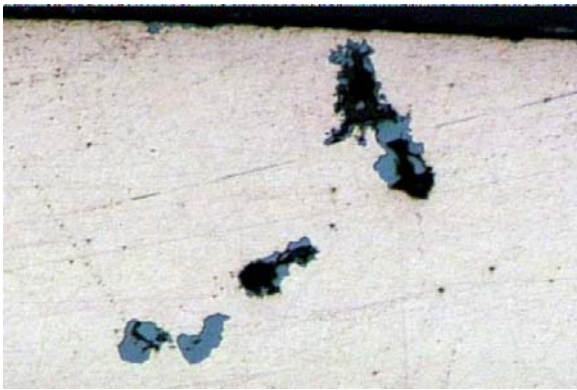
20-ppm



50-Day Formic Acid Test
40/20°C temperature cycle (Tubes are approximately life-size)

	10 days exposure	50days exposure
100-ppm		
50-ppm		
20-ppm		

Typical morphology of Formic Acid



500X, 50-day test, 50-ppm, 40/20°C

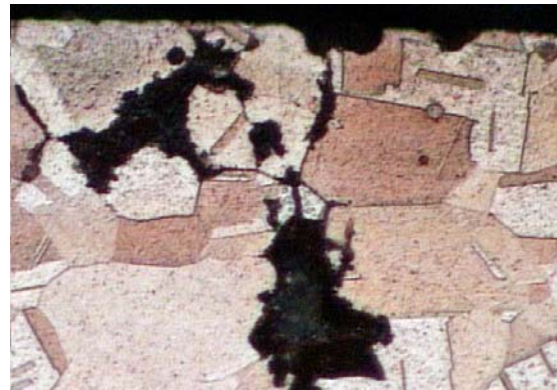


500X six-month, 1,000-ppm 40/20°C cycle,

Atypical morphology of formic acid (obvious intergranular attack)



500X, 50-day test, 50-ppm, 40/20°C, with intergranular attack. See right for etched condition.



1250X etch clearly showing intergranular attack. See left for unetched condition.

Morphology of Acetic Acid

Typical



500X, six-months, 1000-ppm, 40/20° cycle

Atypical (shows branching)

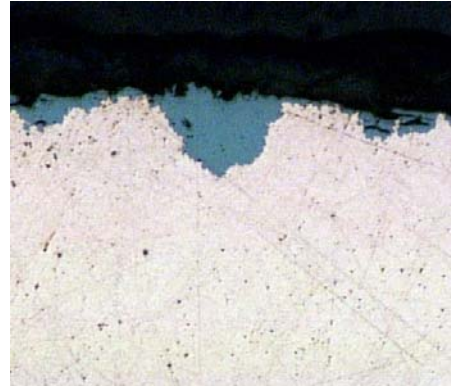


500X, six-months, 100-ppm, 40/20° cycle

Morphology of Formic(20%)/Acetic(80%)



500x six months 1000ppm, 40/4°C



500x six months, 1000ppm, 40/20°C



Ethylene glycol thermally degraded 1250X,
six-months, 40/20°C

The formic/acetic 40/4°C picture is typical of deeper pits at this temperature and at 55/20°C

The formic/acetic 40/20°C picture is typical of those at that temperature.

The ethylene glycol picture is atypical in that it is a well defined formicary pit.

APPENDIX D

STATISTICAL REPORT

D. STATISTICAL ANALYSIS

Statistical analyses generally require estimates of random variability that typically come from experimental replicates, which are easier when factors are nicely crossed. For both of these reasons, the analysis starts with the 70-day data and assumes that the 2-mm distance between samples is sufficient to produce more-or-less independent replicates.

D.1. Seventy Day Exposure

The initial tabulation produced the following results for the seventy day exposure:

STAT TABLE 1.

Effect of solution and temperature regime on formicary pit and density outcomes.

Outcome	Temp (°C)	Acid			Ethylene Glycol		
		Formic	Formic/Acetic	Acetic	1	2C	2U
Maximum pit depth (mils)	55/20	1.0	1.6	1.3	0.2	0	0.1
	40/20	6.0	2.3	2.4	0.2	0.1	0
	40/ 4	5.3	2.0	1.7	0.1	0	0.1
Average pit depth (mils)	55/20	0.8	1.0	0.9	0.2	.0	0.1
	40/20	4.8	1.5	1.8	0.1	0.1	0
	40/ 4	3.8	1.5	1.2	0.1	0	0.1
Pit density (outer surface @ 25x)	55/20	3.8	6.3	8.3	0	0	0
	40/20	9.8	6.6	11.9	0	0	0
	40/4	12.7	4.8	6.0	0	0	0

Note: Outcomes are averaged across the 3 depth replicates. Acid outcomes are averaged across concentrations.

The outcomes are for formicary pitting. The "Average pit depth" is the average of the five deepest observed formicary pits. If fewer than five pits were observed, it is the average of the observed formicary pits.

Pit density is the number of formicary pits observed on one third of a cross-section of the outer circumference at 25X magnification.

The ethylene glycol results are different from the acid results, and appear to be little affected by preparation or temperature and are therefore ignored in the rest of this statistical report

Because there is no 55/4°C temperature combination, it is possible to combine the two temperature variables into one with three values. With ethylene glycol eliminated, acid concentration can be added to the analysis. These results are in Stat Table 2:

STAT TABLE 2.
Outcome versus acid type and concentration.

Outcome	Acid			
	Concentration (ppm)	Formic	Formic/Acetic	Acetic
Maximum pit depth (mils)	100	2.4	0.4	0.5
	1,000	5.7	1.7	1.8
	10,000	-	3.8	3.0
Average pit depth (mils)	100	1.5	0.2	0.3
	1,000	4.7	1.2	1.2
	10,000	-	2.5	2.4
Pit density (outer surface @ 25x)	100	6.8	0.1	1.9
	1,000	10.8	4.9	8.1
	10,000	-	12.7	16.2

Note: Averaged across temperature regimes. The 10,000-ppm formic acid tubes were removed after 14-days and cannot be used in this analysis. The outcomes are for formicary pitting. The “Average pit depth” is the average of the five deepest observed formicary pits. If fewer than five pits were observed, it is the average of the observed formicary pits. Pit density is the number of formicary pits observed on one third of a cross-section of the outer circumference at 25X magnification.

D.1.1. ANALYSIS OF COVARIANCE

Analysis of covariance shows the following statistically significant effects:

- Temperature regime affects outcomes (pitting density is least affected).
- Acid type, acid-temp interaction, and log concentration of acid strongly affect all three outcomes.
- Log concentration of acid increases the outcomes: the regression coefficients are 1.7, 1.3, and 6.4 units per log₁₀ unit. Multiple-R² ranges from .73 to .70. (It is the convention in statistics to report values which could have a maximum value of one without a leading 0, e.g. .70 not 0.70.)

Statistical note: (linear) regression analyzes the (linear) effect of a numerical variable on a numerical output. Analysis of variance does the same for categorical input variables. Analysis of covariance combines both types of input variables. In the present case, acid type and temperature regime are categories while log concentration of acid (and outcomes) are numerical. Log concentration is used because the effect of concentration is much more linear on the log scale than on the raw scale.

D.1.2. CONCENTRATION ADJUSTMENT

Stat Table 2 shows that the experimental design is slightly unbalanced in that there are no samples with formic acid at concentration 10,000-ppm. Since concentration affects outcomes, averages across concentration, as in the acid half of Stat Table 1, are somewhat biased. Stat Table 3 repeats that part of Stat Table 2 after removing the linear effect of log concentration. This is done by increasing the outcomes at 100-ppm and decreasing the outcomes at 10,000-ppm according to the estimated regression coefficients reported above in section D.1.

STAT TABLE 3.
Concentration-adjusted outcome by acid and temperature.

Outcome	Temp (°C)	Acid		
		Formic	Formic/Acetic	Acetic
Maximum pit depth (mils)	55/20	1.6	1.4	1.1
	40/20	6.6	2.1	2.2
	40/ 4	5.8	1.7	1.4
Average pit depth (mils)	55/20	1.2	0.8	0.8
	40/20	5.2	1.3	1.6
	40/ 4	4.3	1.3	1.1
Pit density (Outer surface @ 25x)	55/20	6.2	5.3	7.5
	40/20	15.1	4.0	5.2
	40/4	15.1	4.0	5.2

Note: Adjusted for log concentration. The outcomes are for formicary pitting. The “Average pit depth” is the average of the five deepest observed formicary pits. If fewer than five pits were observed, it is the average of the observed formicary pits. Pit density is the number of formicary pits observed on one third of a cross-section of the outer circumference at 25X magnification.

D.1.3. FURTHER ANALYSIS

Many statistical analyses, including standard analysis of covariance, assume that random variability is about the same for each experimental cell (combination of input factors). For positive measures, this assumption is often false. Typically, cells with higher averages (across replicates) have higher variance. This is true for this study, although the data from the printouts are not repeated here.

One solution is to transform outcome variables by taking square roots or logs. Thus the analysis of covariance was repeated using the log of pit depths and the square root of density. The result is that a) cell variability is more even and less related to cell average, and b) all effects are more obviously significant ($p < 0.01$, usually much less). Multiple-R² is .86 and .88 for pitting (maximum and average respectively) and .77 for pitting density.

Stat Table 3 suggests that most of the temperature effect is due to the change in T-high. Splitting temperature back into two variables verifies this. The effect of T-low is not statistically significant. The p-value varies from .05 to .25 depending on the outcome and exact method of reanalysis.

D.1.4. DAY EFFECT

Prior to seventy days, the design confounds the effect of concentration and days: the 10,000-ppm concentration samples were measured at fourteen to sixteen days while the 100-ppm and 1,000-ppm samples were measured at forty-nine to fifty-one days (plus one at thirty-five days). However, the nearly complete data at seventy-days gives a day-independent estimate of concentration effect that can, in principle, be used to remove concentration effects enough to estimate the day effect.

The final analysis of covariance for this report looked at the effect of T-high, acid type, T-high times the acid interaction, log concentration, and days on the raw and transformed outcome variables. All potential effects are statistically significant (for most, $p < 0.01$), except that days has no effect on density.

For maximum and average pit depth, the estimated regression coefficients are 1.5 and 1.2 for log concentration (slightly less than above) and .023 and .016 (per day) for days. Multiple-R2 is .76 and .78 for pitting and .58 for density.

D.2. AT SIX-MONTHS

The following two tables may be compared with the corresponding Stat Tables (1) and (2) for seventy-days.

STAT TABLE 4.
Effect of solution and temperature regime on formicary pit and density outcomes at six-months

Outcome	Temp (°C)	Acid			Ethylene Glycol		
		Formic	Formic/Acetic	Acetic	1	2C	2U
Maximum pit depth (mils)	55/20	1.3	2.5	2.4	0.2	0	0
	40/20	5.8	3.8	5.3	0.5	0.1	0
	40/ 4	6.4	2.2	2.2	0.6	0	0
Average pit depth (mils)	55/20	1.0	1.8	2.1	0.2	0	0
	40/20	4.1	3.2	4.7	0.3	0.1	0
	40/ 4	4.8	1.7	1.7	0.5	0	0
Pit density (Outer surface @ 25x)	55/20	17.8	10.3	4.6	1.0	0	0
	40/20	13.7	25.8	11.0	0.3	0	0
	40/4	22.4	19.7	7.7	1.7	0	0

Note: Outcomes are averaged across the 3 depth replicates. Acid outcomes are averaged across concentrations. Middle and bottom samples are included. n = 118 (total for all cells).

The ethylene glycol results remain clearly different from the acid results; EG1 is a little higher than before. All ethylene glycol samples were ignored in the rest of this report.

For the (55°C or 40°C)/20°C samples with acetic acid (mixed or pure) the depth (max and average) has about doubled, otherwise, depth has changed less. Pit density is higher except for tubes exposed to acetic acid at 55/20°C.

STAT TABLE 5.
Outcome at six months versus acid type and concentration.

Outcome	Concentration (ppm)	Acid		
		Formic	Formic/Acetic	Acetic
Maximum pit depth (mils)	100	2.9	0.5	0.7
	1,000	6.4	2.0	1.7
	10,000	-	6.1	7.9
Average pit depth (mils)	100	2.1	0.4	0.5
	1,000	4.8	1.5	1.3
	10,000	-	5.0	7.1
Pit density (Outer surface @ 25x)	100	15	2.3	3.2
	1,000	22	35	9.5
	10,000	-	21	11.2

Note: Averaged across temperature regimes. Middle and bottom are included. n = 80 (total for all cells).

The depth of attack has more or less doubled at the 10,000-ppm concentration versus little change at the lower concentrations. All depths except for acetic acid at 10,000-ppm are less than 2.6 (182/70) times their previous value, suggesting that depth increase is tapering off. Density is higher for all samples except acetic acid at 10,000-ppm, the ratio to that at day seventy is quite variable.

D.2.1. REDUNDANT OUTCOMES

As at seventy-days, the average maximum depth at six-months for a particular table cell is consistently around 25% greater than the corresponding average of the average-of-five measurements. Across all 179 acid samples, the correlation between the two measured outcomes is 0.98 (whereas for density versus average-of-5, it is 0.36). A plot of maximum versus average-of-5 shows that there are no extreme outliers, i.e. no samples for which the maximum is drastically higher than the average.

This, combined with the similarity of analysis outcomes for the two variables, suggests that measuring maxima alone would have been sufficient for this study. For future studies, it is recommended that only the two deepest pits be measured. In the discussion below, 'depth' is sometimes used to refer to both maximum and average.

D.3. AT SEVENTY DAYS AND SIX MONTHS

There are 24 experimental jars in the acid branch of the study. Each contained a piece of tube and formic or acetic acid (or mixture) at a particular concentration (8 combinations) and was subject to one of 3 temperature regimes. The section cut off the top of each copper tube was polished to 3 depths at both seventy-days and six-months. The rest of this report summarizes the variance and regression analyses of the 3 formicary pit outcomes for these 144 (24 x 6) samples.

Properly speaking, the measures at the six depths (3 at seventy-days and 3 at six-months) from one tube are 'repeated measures' on that experimental unit. The variable 'days' is a repeated measures factor within that experimental unit rather than an experimental factor between experimental units. A 'proper' analysis would have to take these facts into account, whether or not they ended up making any substantive difference.

There would be difficulties in doing a ‘proper’ analysis due to the absence of experimental replicates and the absence of some combinations of experimental factors (no 10,000-ppm formic acid samples beyond day fourteen, no 55°C/4°C temperature regime). Since the extra work is not obviously justified for the goals of this project, as explained at the top of the seventy day section, this analysis so far treats the repeated measures as if they were replicates. It is believed that the main effect of doing so is to make p values look lower than they should be (and statistical significance higher than it should be). Therefore, this analysis is somewhat compensated by being more strict than normal in what p values are reported as significant.

D.4. FACTOR RANKINGS AND INTERACTIONS

Log concentration (coded 2,3,4; e.g the log of 100 is 2) had the greatest effect on depth, followed by acid (coded 0.0, 0.8, 1.0 for the fraction of acetic acid), temperature regime (due more to the effect of 55°C vs. 40°C rather than 20°C vs. 4°C), and days.

There is a significant interaction between acid and temperature effects. This can be seen in Stat Tables 1 and 4 where 40/4°C samples resemble 40/20°C samples with formic acid, but are more like the 55/20°C samples with acetic acid.

With formic acid samples removed (due the absence of jars with formic acid at concentration 10,000-ppm after day 16), there is an interaction between day and log concentration, which can be seen in the formic/acetic and acetic columns of Stat Tables 2 and 5. At seventy-days, the 1,000-ppm samples (log concentration = 3) are about half way between the 100-ppm and 10,000-ppm samples (log concentrations 2 and 4 respectively). At six-months, the 10,000-ppm samples have much deeper formicary pits than before while the pit depth with the other concentrations are little changed.

For pit density, the results are much the same as with pit depth, except that day is more important than temperature instead of less. There also appear to be more interaction effects.

D.5. REGRESSION RESULTS

Stat Table 6 presents the results of simple multiple linear regression. For readers not familiar with this procedure, this table says that on average, increasing logcon by 1, while holding other variables constant, increases the maximum depth of formicary corrosion by 2.4-mils, average-of-5 by 2.0-mils, and pit density by 6.5-pits. On the other hand, increasing acetic acid from none (only formic acid and deionized water in the test solution) to all (only acetic acid and deionized water in the test solution) decreases outcomes by the amount indicated. RSQ is the fraction of outcome variance explained by these inputs, larger is better. For example, the linear fit of these five input variables accounts for 62% on the variance of maximum depth across the 144-samples. RMSE is an adjusted standard deviation that estimates the typical amount of the outcome not explained by the inputs; smaller is better.

STAT TABLE 6.
Regression coefficients, R square (RSQ), and root
mean square error (RMSE) for seventy days/six month acid samples

Outcome	Input Variable					RSQ	RMSE
	Logcon	Acid	T-hi	T-low	Days		
Formicary max (mils)	2.4	-3.3	-0.15	0.051	0.0106	.62	2.0
Formicary avg (mils)	2.0	-2.5	-0.13	0.046	0.0102	.59	1.7
Density (outer surface @ 25x)	6.5	-8.7	-0.33	0.023	0.068	.37	9.7

Note: see previous section for input variable scaling

The following comments pertain to this analysis:

- Days: treating 'days' as a repeated measure would probably change RSQ and RMSE but leave the regression coefficients about the same.
- 0-intercept terms: predicting outcomes extrapolated to all input variables being 0 is omitted as not sensible for this analysis. The choices of 0 for log concentration and acid type are arbitrary. So is the choice for temperature unless it is extrapolated to absolute 0 (which here would give negative pit depths and pit densities). At 0 days, pit depths and pit densities were presumably 0.
- Linearity: this procedure assumes that input variables with more than two values have a linear effect on outcomes. For logcon, this is reasonable at seventy days but much less so at six months. For acid, the outcome for the mixture of formic and acetic acids is often either lower or higher than both formic acid and acetic, rather than in between (and closer to acetic acid) as expected (and fit) by linearity.
- Interaction: this procedure assumes that the effect of the different input variables is additive, which is to say that there are no significant interactions between them. As described in various places above, there are significant interactions.
- Weighting: this analysis assumes that the experimental variability is independent of outcome value and that all samples should be given the same weight. As discussed in the seventy day section, this is typically not true, as in this study, for outcomes whose range is comparable to their maximum.
- Improvements: an improved (better fitting) regression model can be developed using some combination of the following: add product terms to the linear model; switch to a nonlinear model; transform the outcome variables (as was done for the analyses of variance); and/or give samples unequal weights.

A number of questions were raised and answered in Appendix E.

APPENDIX E
ANSWERS TO QUESTIONS RAISED ON THE
STATISTICAL REPORT

E. Answers to Questions

Q1. Compared to other similar analyses, how would you verbally characterize the r- square values of .59 and .62 shown for average pit depth and deepest pit?

A1. Subject to the caveats noted in the report, the overall results are considered to be very good. The specific r-square values can be classed as average to good, but on the basis of inadequate directly comparable experience.

For nonlinear models with one experimental factor, such as time or dose (but usually not both together), it is preferred that r-squares are at least .7 and preferably over .8. For lower values, the important question is whether the non-fit mostly consists of 'random noise', either from the experimental system or the measuring process, or systematic deviations due to not using the 'right' model. In this case, there are nonlinear interactions that could be brought into the model to boost the r-square values, but there is also noise.

Many multifactor analyses are concerned with true categories and analysis of variance, where the focus is on individual factors and their interactions. Overall R-squares are either not calculated or ignored because the experimenters are not concerned about such.

Q2. I would like you to evaluate these statements: Acetic acid provides more predictable results, at six months, as concentration is increased.

A2. This question preferably refers to Stat Table 5, column 'Acetic'. The actual numbers for average-of-5 depth from the data table that was received are in Stat Table 7.

**STAT TABLE 7.
Avg-of-5 depths and relative deviations
for acetic acid at six months**

Concentration (ppm)	Temp (°C)	Avg Formicary Pit Depth (mils)			Relative Deviation
10k	55/20	5.0	5.2	5.7	12%
	40/20	11.8	11.2	10.8	8%
	40/4	4.3	4.1	5.5	25%
1k	55/20	0.8	0.6	0.7	25%
	40/20	2.3	1.5	1.4	39%
	40/4	1.7	1.4	1.5	17%
100	55/20	0.4	0.3	0.3	25%
	40/20	1.2	1.0	1.2	17%
	40/4	0.3	0.4	0.3	25%

% = range of 3 / largest

If “predictable” means absolutely predictable, then the answer is the opposite: the three repeated measures for samples at 10,000-ppm are more variable and less predictable. As noted in the statistical analysis on the seventy day data (Appendix D.2), this is completely normal. If predictable means relatively predictable (standard deviation / mean, for instance, which was quickly approximated by range/ largest), then the 10,000-ppm samples are, overall, the best.

If predictable means 'most useful for studying the effect of other factors' (such as temperature regime in this example), then the statistical issue is whether the outcome is large enough for differences to be visible. In particular, how large are the (relative) differences between treatments in relation to the (relative) differences within treatment (here, the three repeated measures). For this, 10,000-ppm is better than 1,000-ppm but not much better than 100-ppm.

The practical issue is that knowing that a factor affects small outcomes that do not matter much is less useful than knowing that the factor affects large outcomes that are of concern. So if you want to do a future experiment with one dose, the highest would be recommended.

Q3. [Evaluate...] Pit density is not a suitable outcome metric.

A3. It is definitely statistically less well behaved in this experiment. Unless there is a definite reason to determine pit density, this would not be recommend in future work.

APPENDIX F
FORMICARY CORROSION LITERATURE REVIEW

F. FORMICARY CORROSION LITERATURE REVIEW

F.1. Early references to formicary corrosion.

Notoya (1993) refers to a 1965 report by Keyes that described five cases of formicary corrosion. Pitting with this morphology was discussed by Edwards et al (1977), after studying copper tubes that were pressure tested with antifreeze, stored for a year, and had numerous small leaks after installation. Notoya (1990) draws morphological comparisons to “keloid” corrosion in Be-Cu alloys, “red plug” corrosion in silver-plated copper wires, “directional pitting” in Alloy 20, and “bronze disease.” In the late 1940’s, Evans (1960) analyzed and treated museum artifacts that had displayed “bronze disease” following exposure to acetic acid vapors from wood shavings.

F.2. Failure analysis

Edwards (1977) investigated the failure of 19-mm diameter copper tubing with aluminum fins in the chilled water units an air conditioning unit of a large public building; leaks were evident during installation when the unit was pressure tested with water. The end-capped tubes had been in storage for a year before installation and had been wrapped in plastic. The manufacturer had pressure tested the tubes at the factory with an antifreeze solution. A label left on the tubes stated there could be residual antifreeze solution inside. The pitting started on the inside surface which was reported to be “blue-black to rusty” in color. With an SEM (scanning electron microscope) Cu, Fe, and lower amounts of P, S, Ca, and Cl were found. The source of the Cl was unknown. Micrographs showed branched pitting, which Edwards attributed to the breakdown of the residual fluid.

Yamauchi et al (1983) reported twenty-three (23) cases of formicary corrosion in phosphorous deoxidized copper JIS H3300 (UNS C12200) over a fifteen year span. Nine of these events occurred before commissioning, and all occurred no more than two years after commissioning. The failures were almost evenly divided between failure initiated from the inside (twelve) and from the outside of the copper tubes (eleven). Eight of the eleven inside initiated failures occurred before commissioning. Electron probe microanalysis (EPMA) performed on the outside surfaces of seventeen of the tubes found Cu, O, Cl, Fe, and S. EPMA analysis performed on the pits on thirteen tubes found only Cu and O, except for one instance of Cl. X-ray diffraction (XRD) of the surface corrosion products on six of the tubes identified the presence of one or more of CuOH , Cu_2O , CuO , $(\text{Cu}_4\text{Cl}(\text{OH})_7)_2 \cdot \text{H}_2\text{O}$, and $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$. The breakdown of residual chlorinated hydrocarbons used in manufacturing was suspected as the corrodant. Reproduction tests were performed (see below).

Notoya et al (1989) recorded an additional twenty-one cases of formicary corrosion during the period of 1983 to 1987. All of these failures were in phosphorous deoxidized copper; five failures were from the inside and the rest from the outside. Three failures were attributed to 1,1,1-trichloroethane, two to the refrigerants, and one each to organic solvent, acetic acid, vulcanized rubber, formic acid, and antifreeze. The corrodant in the remaining eleven cases was not determined. Work was cited presenting fluoroborate in brazing flux and fluoride in lubricants as possible sources of formicary corrosion.

A case attributed to acetic acid, which occurred in a sushi bar, is described in some detail. Notoya noted that additional failures have occurred in sushi bars. The heavy use of vinegar, which is largely acetic acid, in sushi bars prompted Notoya to consider this an instance of failure caused by the environment of the end user. Notoya did lab experiments with acetic acid and other carboxylic acids that established their role as agents of formicary corrosion. The pitting was concentrated in the U-bends of the tubing and under the aluminum fins. The tubing was type JIS H3300 (UNS C12200) with an OD of 9.52-mm and a wall thickness of 0.80-mm. EPMA of the pits detected C, O, Ca, and traces of S, F, and Cl. The halogens (Cl, F) were attributed to leaking refrigerant. The S could not be accounted for and the carbon is thought to have been from the acetic acid.

Notoya (1990) presented tables with sixty-four failures that occurred between 1978 and 1988. These failures were obtained from questionnaires sent to manufacturers by the Corrosion Committee of the Japan Copper Development Association (JCDA). Failures initiated on the inside in 33% of the cases and on the outside in 55%. The initiation sites for the remaining 13% were unclear. Soldered areas accounted for 5% of failures, 53% occurred in straight tubes, and 42% in bent areas. Notoya concluded that the failures followed a random distribution; he introduced a descriptive nomenclature for the formicary morphology.

Isobe et al (1992), increased the number of tabulated failures to one hundred and one. The new data slightly changed the percentages presented above: inside 34%, outside 60%, unknown 6%; solder 3%, straight tube 66%, and bent tube 31%. Isobe (1992) later described a method of finding the pits in failures that involved briefly dipping the tube in acid to remove the scale and then testing with a dye penetrant.

Takahashi et al (1992) reported a failure investigation where no chlorinated solvents had been used, only self-evaporating lubricating oils. This study initiated from an American air conditioner manufacturer who found numerous leaks during pressure testing prior to shipping. The copper used was JIS H3300 (UNS C12200). Two of the eight leaks found in one section of tube were in the U-bend areas of the tubes. Four different oils (two evaporative oils and the other two non-evaporative oils) were assessed (see section F-3).

Hoffman (1998) reported on the failure of UNS C12200 tubing in the evaporator of a new chiller. The unit was drained for the winter (but not dried) and treated with glycol. Two months later, numerous leaks caused by formicary corrosion were detected. All of the leaks occurred on the inside, and the majority of the leaks started on the crests of the internal rifling. Formicary corrosion was not associated with the lap marks in the rifling. The attack was ascribed to possible traces of trichloroethane remaining from the cleaning of the tubes, or to the breakdown of uninhibited glycol to organic acids.

Elliott and Corbett (1999) reported on two failures. The first failure was in heat exchanger bundles that developed formicary corrosion on the inside in as little as two months service. The suspected agents were traces of bromoform, bromodichloromethane, and dibromochloromethane derived from water used to cool the brazed assemblies. The authors concluded that these chemicals decomposed to formic acid, which caused the attack. To prevent future attacks, an activated carbon filter was installed to improve water quality and efforts were made to keep the tubes dry; no further cases were reported.

The second case was the failure of a commercial air conditioning system within a year of installation where pits originated on the inside surface. The causative agent was believed to be a synthetic water-based drawing/finning lubricant that had not been totally removed during cleaning.

Kelly et al (2000) reported formicary attack in the chilled water system of an eight story building. The original leak occurred six years after installation and damaged office materials. The phosphorous deoxidized copper tubing displayed formicary corrosion, which had initiated on the outside; green corrosion products were observed on the outside. Polystyrene foam was used as insulation and was glued to the pipe with a sealant manufactured from fish oil. The insulation in the area of the leak had a pH of 3.4. It was thought that the copper acted as a catalyst for the breakdown of the fish oil to organic acids. Radiography of pipes still in service found pitting in 30% of the areas examined. Following a second leak six months later, thermographic imaging was utilized; the technique offered simplicity, speed, and greater flexibility. Cold spots were found in about 5% of the tested lengths. Samples of the adhesive, green corrosion products, and the insulation at a cold spot were tested for the presence of organic acids. Very high levels of formic acid were found (4,700-ppm in the green corrosion product and 2,200-ppm in the adhesive). The ratio of formic acid to acetic acid was consistently between 3.6 and 3.9. It was concluded that the vapor barrier was penetrated by moisture, which allowed condensate to form on the pipes that led to the decomposition of the adhesive. The formic and acetic acids produced by this decomposition led to the failures. Kelly opined that the tenacity of formicary corrosion may necessitate the replacement of copper in the HVAC industry with another material.

F.3. Procedures used in laboratory testing

Yamauchi et al (1983 [published in Japanese, summarized in English by Notoya et al (1988)]) tried to produce formicary corrosion in a laboratory setting. A test matrix was developed in which three mg of commercial 1,1,1,-trichloroethane was mixed with one mL of tap water and/or one mL of machine oil, and one gm of iron or copper oxide powder and placed in copper U-bends. The U-bends were 250-mm long with a radius of 50-mm, an OD of 9.52-mm, and a wall thickness of 0.35-mm. The ends of the copper tube were sealed and the tubes were heated to either 150°C or 400°C for five minutes and exposed for up to twenty-one days at room temperature. Formicary corrosion was found in some of the tubes after seven days.

Notoya et al (1989) found formicary corrosion in copper tubes from a sushi bar and suspected acetic acid from the vinegar present. To test his hunch he did laboratory tests with six carboxylic acids:

- formic HCO_2H
- acetic $\text{CH}_3\text{CO}_2\text{H}$
- propionic $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$
- n-butyric $\text{CH}_3(\text{CH}_2)_2\text{CO}_2\text{H}$
- n-pentanoic $\text{CH}_3(\text{CH}_2)_3\text{CO}_2\text{H}$

The laboratory test consisted of a copper tube 100-mm long, with a 9.52-mm OD and a 0.4-mm wall thickness in a test tube in a closed one liter glass jar. The test solution was 100-mL of deionized water with 1% volume of the selected acid. The copper tube was exposed in the vapor phase. Oxygen was added at the start of the test which was performed at room temperature.

After forty days all of the tubes were corroded and only formic acid produced the branched morphology of formicary corrosion. Acetic acid pits had a semicircular appearance. The most pronounced pitting was found with the formic acid. Acids with larger molecular weights displayed progressively less attack. Notoya noted that the behavior was in accord with the dissociation constants. At acid concentrations greater than 1% volume, only general corrosion occurred.

Notoya (1990) reported additional laboratory tests. Copper tubes exposed to the vapor of the liquid from crushed ants or ginkgo nuts did produce formicary corrosion. A copper tube exposed to the vapor of boiling hydrofluoric acid for one second and then put in a jar with water and oxygen for a month developed formicary corrosion; repeating the one second exposure with HCl, H₃PO₄, HNO₃, and H₂SO₄ caused no formicary corrosion.

Hamamoto and Imai (1991) performed reflux hydrolysis on four hydro-chlorinated organic solvents:

- 1,1,1-trichloroethane CH₃CCl₃
- trichloroethylene CHCl=CCl₂
- methylene chloride CH₂Cl₂
- tetrachloroethylene CCl₂=CCl₂

Acetic acid was detected after the hydrolysis of the 1,1,1-trichloroethane but not in the other three cases. More tests were conducted with the former solution and more acetic acid was produced following a longer exposure time with additional water. Samples of these four chemicals obtained from different manufacturers had similar results; formicary corrosion was only found in tests run using the hydrolyzed 1,1,1-trichloroethane.

Isobe et al (1992), wrote of further tests using Notoya's procedure (copper tube placed in a test tube in a one liter glass jar with 100-mL of test solution, and added oxygen); the copper was phosphorous deoxidized JIS H3300 (UNS C12200) which was bright annealed. The following variables were tested: gas added (nitrogen or argon); thermal cycle (constant 20°C or 30°C, and twelve hour cycles of 25°C/40°C or of 15°C/30°C); and 1% of corrodent (formic acid, acetic acid, formaldehyde, and acetaldehyde). Some formicary corrosion was found in the nitrogen atmosphere; less was found in the argon; the authors believed the oxygen (air) was not totally displaced during these tests. Acetic acid produced the rounded pits reported above; formaldehyde and acetaldehyde both had a morphology like formic acid. The formicary attack observed during a constant 30°C test was more severe than at a constant 20°C. Thermal cycling was more severe than either constant temperature; but the authors did not distinguish between the two thermal cycles used.

Nagata (1992) reported further progress from the Corrosion Committee of the JCDA. Tests using formic acid were run with phosphorous deoxidized (JIS H3300, UNS C12200) and oxygen-free copper (JIS H3300, UNS C10200) with different surface finishes (bright annealed, polished, pickled, or oxidized in air at 150°C for ten minutes). More formicary corrosion was seen with the UNS C12200 copper. Nagata concluded that water and oxygen are essential to produce formicary corrosion.

Isobe (1992) described a complex set of laboratory experiments that were intended to more accurately replicate field conditions. A loop of UNS C12200 tubing was connected to a chiller and run through a transparent vessel (glass or acrylic). The copper tube was degreased and pickled prior to testing. Deionized water at the bottom of the vessel was in contact with a portion of the tube. There was a hole at the top of the vessel that could be closed. The top and bottom of the vessel had stoppers made of silicone rubber or fluororubber. The flow of cooling water through the tube was continuous, intermittent, or none. The air tightness of the vessel was varied. All tests were run for forty-three days at room temperature.

The testing was done in two parts, Part A and Part B. Part A used deionized water in all fourteen of its tests, using the variables mentioned above. It was the intent of Part A to find iterations which did not cause formicary corrosion or other types of corrosion. Then the conditions of one of these iterations were used in the fourteen tests of Part B, which replaced the deionized water with four different chemicals (formic acid, acetic acid, trichloroethylene, and 1,1,1-trichloroethane at different concentrations).

Two of the fourteen tests in Part A did not produce corrosion in that portion of the tube exposed to the vapor of deionized water; both of these used a glass vessel and fluororubber stoppers. The use of an acrylic vessel and/or silicone rubber stopper always resulted in corrosion in the vapor phase, which was usually formicary corrosion.

Formicary attack was seen on the immersed part of the copper tube in many of the iterations, including the two tubes that had not been attacked in the vapor phase. Isobe notes that this was the first reported instance of formicary corrosion in the liquid phase. The attack was much shallower than that usually seen in the vapor phase.

Part B of the test used intermittent flow through a tightly closed glass vessel fitted with a fluororubber stopper. Using deionized water as a control, various percentages of formic acid, acetic acid, trichloroethylene, and 1,1,1-trichloroethane were tested. Formicary corrosion was clearly seen in the vapor phase with formic acid, acetic acid, and 10% volume 1,1,1-trichloroethane. In the liquid phase, formicary corrosion was reported in the copper exposed to the deionized water and to the 1% trichloroethylene solutions.

Isobe noted that the increased presence of formicary corrosion when the coolant was flowing and the vessel was tightly sealed correlates with increased dew formation; furthermore acrylic and silicone rubber should be avoided. (No explanation was offered for the attack in the liquid phase).

Takahashi et al (1992) reported testing four different oils. Tests were done with two evaporative oils ("A" and "B") and two non-evaporative oils ("C" and "D"). Oil "A" was used by an American manufacturer that had experienced failures, but had not used chlorinated hydrocarbons (considered as likely agents for formicary corrosion) and oil "D" had reportedly caused formicary corrosion. The oils were applied to copper plates and kept at 50°C for 7-days, then the weight loss was determined. A residue comprising 10% of the initial weight of oil A was identified as polyalkyleneglycol. [Note: polyalkyleneglycol is used to improve lubricity and is reported to easily breakdown to formic acid in the presence of water.]

Samples of each oil were mixed with equal volumes of deionized water and heat refluxed for 10-days. The pH of all samples dropped from the 8-6 range down to the 6-3 range. The non-evaporative oils, "C" and "D", had less of a pH change than the self-evaporative oils, "A" and "B". The hydrolyzed oils were analyzed for levels of formic and acetic acids using IC; oil "A" had 660-ppm and 510-ppm, oil "B" had 880-ppm and 700-ppm, oil "C" had 180-ppm and 300-ppm, and oil "D" had less than 1-ppm of each respectively. Pre-hydrolysis levels of formic and acetic acids in the oil samples were not reported.

As-received oils were mixed 1:1 with deionized water and tested without hydrolysis for comparison with the hydrolyzed oils. One mL of each aqueous oil test solution (hydrolyzed and as-received) were placed inside JIS H3300 (UNS C12200) tubing (300-mm long, 9.52-mm OD, 0.35-mm wall thickness). The copper tubes were sealed and then shaken. Some tubes were placed in the sun (10°C to 36°C) and some in the shade (10°C to 24°C) for one and three months; a 1% volume formic acid was used as a control. At the end of each test the tubes were cut open and the inner surfaces examined for the presence of formicary corrosion. Metallographic cross-sections were also prepared. The formic acid caused formicary corrosion in the sun and shade for both time periods.

The oil "A" test solution, both hydrolyzed and as received (mixed 1:1 with deionized water), developed formicary corrosion in all cases except for the 1-month as-received shade sample, which developed a different type of corrosion. All sunlight samples of oil "D" solution caused formicary corrosion. The 3-month shade exposure of the refluxed sample of oil "D" caused formicary corrosion. Oils "B" and "C" did not cause formicary corrosion.

That only a few spots of formicary corrosion were found with oil "D" is attributed to its viscosity. Oil "D" was presumed not to have wet the tube inside, but just to have left drops in a few locations. The authors stressed that lubricant oils and water may cause formicary corrosion under normal environmental conditions. There are some discrepancies in these results, which may reflect surface tension/viscosity influences. That oil "D" had less than 1-ppm of carboxylic acids after being hydrolyzed was expected to produce zero formicary corrosion. The reason that oil "D" caused formicary corrosion with less than 1-ppm of either formic acid or acetic acid was not explained; or why oils "B" and "C", with levels over 100-ppm did not. Although not stated, there may have been influences from chemicals or stoppers in the equipment.

Miya et al (1993) reported testing lengths of phosphorous deoxidized copper tubing supported horizontally in a 1-L glass test vessel with silicone rubber; the lid gasket was also silicone rubber. (As mentioned above, Isobe (1992) reported that silicone rubber contributed to formicary attack.) The test solution was one hundred mL of 1% volume formic acid and oxygen gas was blown into the vessel for one minute before it was sealed. The vessel was cycled every twelve-hours between 25°C and 40°C for thirty-days. The inside of the formicary pits was analyzed with an SEM and an EPMA. The corrosion products on the outside of the copper tube were scraped off with a glass spatula and dissolved in nitric acid before analysis using IC and inductive bonding plasma emission spectrography. Formate ions and copper ions found in the dark green crystals on the outside of the tube were identified as cupric formate; copper oxide was found in the pits. The absence of carbon suggested that there were no copper formate complexes inside the pits.

Nagata and Kawano (1994) reported laboratory results of a two part test. In the first test, 5-grams of the oil were mixed with 50-mL of distilled water and refluxed for 24-hours; duplicates were used. In this test, a pH drop coincided with an increase in formic acid. Although the formic acid results of the first test were reported in the same table as the second (corrosion test) detailed in the next paragraph, it was for reference only. The actual formic acid levels in the second test were not reported.

The second test attempted to simulate brazing conditions (high temperature hydrolysis) and used hairpins of phosphorous deoxidized tubing that had been manufactured with 100% isoparaffin oil. The copper tubes were tested as-is. Three-mL of an oil and water sample (in the ratio of 1:9) were introduced inside the hairpins. The tubes were sealed and heated to 150°C or 400°C for five minutes and subsequently kept at room temperature for three weeks. Oxygen gas was added to some of the copper tubes before resealing. The copper tubes were maintained at room temperature for a further one to three-weeks. The first oil, which had formic acid from 700 to 900-ppm when hydrolyzed, developed formicary corrosion after both the 150°C and 400°C treatments. This oil was said to be American made and had previously caused formicary corrosion. The creation of formic acid was stated not to be from the paraffin-based oil but was derived from degradation of an added ester. The second oil was a 100% isoparaffin oil, which did not develop formicary corrosion. When the second oil was also tested with an unidentified lubricant added to it, slight formicary corrosion was seen. Analysis found a maximum formic acid level of 43-ppm following the 150°C test conditions. Tests with a third oil with oxygen developed formicary corrosion with the 400°C exposure. The third oil samples had a maximum formic acid level of 13-ppm.

Nagata recommends that both the hydrolysis and the copper tube exposure tests should be used when evaluating oils. The key point is that using only 100% isoparaffin oil, without organochlorine solvents, resulted in no formicary corrosion.

Baba and Kodoma (1995) reported an experiment in which organochlorine solvents were broken down with a thermal treatment and an ultraviolet treatment. These solutions were then used in corrosion tests. The test setup included a standard 1-L glass jar with 100-mL of solution. The control used formic acid and acetic acid at the 1%, 0.1%, 0.01%, and 0.005% levels. JIS H3300 (UNS C12200) tubes were positioned in glass test tubes at a 45° angle. The top 8-mm of the tubes protruded above the glass test tubes and was in direct contact with the test vapor. The vessels were first purged with oxygen and then run for 40-days. The tube surfaces were characterized using XRD, and infrared analyses (FTIR). The test vapor was collected on alkaline filter paper, soaked in distilled water, and evaluated using IC. The following solvents were hydrolyzed:

- 1,1,1-trichloroethane
- trichloroethylene
- tetrachloroethylene
- methylene chloride.

A 0.19-dm³ aliquot of the solvent was mixed with 10-dm³ of deionized water and heat refluxed for 48-hours using a water-cooled condenser. An equal amount of deionized water was then added and an extract tested using IC; electrical conductivity and pH were recorded. Some of the fluid was placed in a quartz cell and exposed for 48-hours to UV light at an intensity of 30-W/m²

obtained with a xenon lamp. The tarnish on the control tubes was Cu_2O and the surface corrosion products were copper (II) formates or acetates. Copper (I) compounds were not observed. Higher levels of formic and acetic acid were produced in hydrolysis that used a higher ratio of water and ran for a longer time. The UV radiation increased the levels of formic acid and decreased those of acetic acid. The 1,1,1-trichloroethane produced the highest levels of carboxylic acids. The degraded solvents were used in corrosion testing after diluting them 50% with deionized water. The more aggressive formicary attack in the samples exposed to UV light is attributed to the increased levels of formic acid. An English translation of the publication implies that all four solvents caused formicary corrosion, but this is not clear. A previous report (Hamamoto and Imai, 1991) had said only the 1,1,1-trichloroethane caused formicary corrosion.

Miyafuji et al (1995) described testing of various copper alloys (in following Table) in 1% (volume) of formic acid for 10 to 40-days; only the graphics and abstract are in English.

	Weight percent alloy	Weight percent Phosphorous
Copper	0.49% Tin	---
Copper	0.48% Aluminum	---
Oxygen Free Copper	---	---
Copper	0.48% Zinc	---
Copper	0.45% Manganese	---
DHP copper	---	0.023
Copper	0.22% Manganese	0.025
Copper	0.48% Manganese	0.025
Copper	0.96% Manganese	0.022
Copper	1.95% Manganese	0.027

A closed 1-L glass vessel was used with 100-mL of the test solution. Unlike previous tests an inner open glass vessel was used to support three glass test tubes vertically; this inner vessel was free of liquid. A section of copper tube was placed vertically in each glass test tube. Deionized water was also in each glass test tube in contact with the bottom third of the copper tube. The temperature cycled at 25°C for six-hours before changing to 40°C for six-hours and then restarting the cycle. A 15-mm long section of the copper tube on either side of the water line is defined as the observed section. A cross section was taken near the top of the tube.

One series of tests looked for a relation between the severity of formicary attack and the amount of phosphorous in the tubes at 0%, 0.05%, and 0.022%. The phosphorous-free alloy had fewer pits and their depth was less than half that of pits found in the 0.022% alloy. Another series of tests compared oxygen-free copper alloyed with additions of Mn (0.45%), Mg (0.31%), Zn (0.48%), Ni (0.47%), Si (0.49%), Al (0.48%), and Zn (0.49%). The Mn alloy had the shallowest formicary attack after 10, 20 and 40-days. The unalloyed oxygen-free copper was in the middle range of attack, and the Sn containing copper tube fared the worst. A series of tests with different amounts of Mn found the most effective at preventing formicary corrosion was the highest tested alloy with 2% Mn. The same results were found when hydrolyzed oils were used in place of the formic acid. A final series of tests compared the alloy with 2% Mn against de-oxidized low phosphorous (DHP) (0.023 weight %) copper alloy. As the test proceeded, the pH of the deionized water in both test tubes dropped, but the pH for the DHP copper alloy dropped farther.

Lower levels of Cu ions were found in the deionized water of the Mn-alloyed copper tube than in the low phosphorous copper tube. The reduced severity of attack is attributed to the Mn ions raising the pH of the corrodent and to formation of a denser corrosion product in the pits, which limited access to the anodic surface.

Notoya (1997d) reported testing condiments containing vinegar (which contains acetic acid). Formic and acetic acids were tested at 1% volume, as were the aldehydes formaldehyde and acetoaldehyde. Grain vinegar, rice vinegar, lemon juice, Worcester sauce, french dressing, vegetable oil dressing, and mayonnaise were also tested. A length of UNS C12200 tubing was suspended in a test tube on an acrylic line. The test tube was sealed with a silicon rubber stopper and kept at 25°C for one and three months. No localized attack was seen with deionized water or with the rice vinegar. The most aggressive attack was caused by the formic acid and the acetoaldehyde. The grain vinegar caused formicary corrosion. The french and vegetable oil dressings caused superficial formicary corrosion. The Worcester sauce, mayonnaise, and lemon juice caused surface pits, but not formicary corrosion.

The same year Notoya (1997a) mentioned work by Chou et al in which formicary corrosion resulted following exposure to small levels of methanol, ethanol, and acetone. Notoya noted that attack was not caused with 50% levels of alcohol and recalled a single instance of reported attack from a sake distillery which was traced to aluminum tape that contained formic and acetic acids. This instance was of interest as it was one of the few failures which showed a formicary morphology with obvious intergranular attack (Notoya 2001B). Notoya suggested that these results warranted more confirmation.

Notoya (1997c) also reported testing UNS C12200 tubing with six different aldehydes for ninety days. The aldehydes tested were:

- Formaldehyde HCHO
- Acetoaldehyde CH₃CHO
- Propionaldehyde C₂H₅CHO
- l-heptanol C₆H₁₃CHO
- l-dodecanol C₁₁H₂₃CHO
- benzaldehyde C₆H₅CHO

The copper tubing was heat treated for 30-minutes at six different temperatures (300°C, 400°C, 500°C, 600°C, 700°C, and 800°C). This test sought potential differences in the copper metal grain size that could cause varying degrees of attack. Since the grain size did not affect the results, Notoya stated that the mechanism was not linked to intergranular attack. Tests were done at room temperature, with the tube suspended over 100ml of liquid containing 1% volume of the selected aldehyde. The first three listed aldehydes caused comparable levels of formicary attack followed by the fifth and then the fourth. The sixth, benzaldehyde, caused no attack, which Notoya noted as consistent with the use of some of its derivatives as an inhibitor for copper. Notoya believed the other aldehydes were oxidized to create organic acids, previously shown to cause formicary attack.

Elliott and Corbett (1999) report on a laboratory test that produced formicary corrosion on UNS C12200 tubing using hydrolyzed synthetic drawing/finning lubricants. Five oil samples were heat refluxed for 48-hours. The copper tubes were placed in glass test tubes inside 1-L mason jars which held the solutions of interest. The test was run for thirty days at 40°C. One of the unidentified fluids caused general corrosion, one fluid caused spherical pits, and the remaining three fluids caused formicary corrosion.

In the same year Ueda and Isobe (1999) reported tests involving heat-refluxed fluids. The self-evaporating lubricant oils were mixed with nine times as much deionized water and refluxed for 48-hours. The copper tubing was placed in a glass test tube in a 1-L mason jar which held 100-mL of the test fluid. A correlation was reported between the pH of the test fluid and the occurrence of formicary corrosion; a hydrolyzed fluid with a pH above five was unlikely to cause attack. However, the researchers believed the copper tube exposure test should be performed even when the pH was above five.

Notoya (1999) published further test results. Because some failures were occurring in rooms with wood paneling; aldehydes, ketones, α -pinene, formic acid, methylformate, and sawdust from 8-different wood species were tested. JIS H3300 (UNS C12200) copper tubing was suspended in a 1-L glass jar which held 100-mL of deionized water and 150-grams of sawdust or one volume percent of a chemical. Testing was for one and three-months. Tested materials:

Corrodent	Formula	Corrodent	Formula
Formic acid	HCOOH	Formaldehyde	HCHO
Propionaldehyde	C ₂ H ₅ CHO	Methylformate	HCOOCH ₃
1-hexanal	CH ₃ (CH ₂) ₄ CHO	1-heptanal	CH ₃ (CH ₂) ₅ CHO
1-octanal	CH ₃ (CH ₂) ₆ CHO	1-nonanal	CH ₃ (CH ₂) ₇ CHO
1-decanal	CH ₃ (CH ₂) ₈ CHO	1-dodecanal	CH ₃ (CH ₂) ₁₀ CHO
α -pinene	C ₁₀ H ₁₆	Acetone	CH ₃ COCH ₃
2-butanone	C ₂ H ₅ COCH ₃	3-methyl-2-butanone	CH ₃ COCH(CH ₃) ₂
2-hexanone	CH ₃ CO(CH ₂) ₃ CH ₃	4-methyl-2-pentanone	(CH ₃) ₂ CHCH ₂ COCH ₃
2-heptanone	CH ₃ CO(CH ₂) ₃ CH ₃	Sachalensis	Wood
P. jezoensis	Wood	L. leptoleptis	Wood
Q. crispula	Wood	F. mandshurica	Wood
Maxowicziana	Wood	K. pictus	Wood
U.davidiana var. japonica	Wood		

Formicary corrosion occurred within three-months by formic acid, P. jezoensis (a wood), and methylformate. Formaldehyde and propionaldehyde produced branched pitting, not classic formicary corrosion [sic]. The remaining substances caused either general corrosion or pitting with a very slow growth rate.

Cano et al (1999) report on formicary testing which was prompted by the failure of an air conditioning unit after three months. Phosphorus deoxidized (0.019-0.022%P) tubing like that which had failed was used, as was tubing with higher concentrations of phosphorous (0.020-0.035 and 0.03). Two different self-evaporating synthetic ester based lubricants were examined; one which was used for stamping the aluminum fins and the other for bending hairpins and expanding the copper tube.

The three types of copper tubing were soaked in the selected lubricant for 5-days. Then the ends were flattened and the tubes dried with hot air. The specimens were split open and then exposed to three levels of relative humidity (100%, 80%, or 40% per ASTM E-104) in an airtight glass vessel. The vessels were kept at 20°C or 40°C for at least fifty-days. There was a control that did not expose the tubing to the oils. Instead this tube was heated with an oxyacetylene torch. Analysis of the corrosion products on the control did not show the organic acids, Cl, and S seen in tubes treated with the lubricants. The corrosion products observed on the tubing from the failed air conditioner were also found on the new tubes tested after treating with lubricant oil. Surprisingly, no cross sections were prepared so comparisons of formicary pitting were not made.

Corbett and Elliott (2000) reported tests with hydrolyzed oils and UNS C12200 copper. A 40/25°C temperature cycle was used (8-hours low and 16-hours high on weekdays, always high on weekends). The test vessels were purged with ozone at the start of the test. The test ran for 90-days. Both of the finning fluids tested produced formicary corrosion with branched tunnels, as did one of the drawing fluids. The other drawing fluid produced circular pitting.

Notoya (2001c) reported on tests conducted with juice from the fruit of the ginkgo nut. JIS H3300 (UNS C12200) copper tubing was placed in a test tube in a 1-L glass vessel. A 100-mL aliquot of test fluid (containing 1, 5, 10, 50, or 100-volume % of ginkgo juice) was also placed in the test vessel for the test which lasted for one and three-months. Ginkgo juice contains acetic acid and formicary corrosion was seen in all samples after three-months. The higher the concentration of ginkgo juice used the more severe the attack.

The results from the work performed under this ARTI project have been summarized and presented before members of the corrosion industry (Corbett 2004).

F.4. Preventive measures

Most researchers have recognized that the presence of oxygen, water, and a specific type of organic corrodent are all required to produce formicary corrosion on copper and copper alloys. Eliminating any one of these will prevent or reduce the propensity for this attack.

Edwards et al (1977) suggested that “thorough rinsing and drying of the tubes before plugging, coating the tubes with a more adequate inhibitor (type not indicated), or possibly shipping the tubes full of inhibited antifreeze to prevent the ingress of air,” would be beneficial.

Yamauchi et al (1983) endorsed “(a) avoiding the coexistence of chlorinated hydrocarbon and water, (b) avoiding prolonged contact of copper tube with chlorinated solvent... (c) removing chlorinated hydrocarbon before heating of copper tube, and (d) selecting a well stabilized solvent,” to reduce formicary corrosion.

Notoya et al (1989) noted the beneficial changes for a manufacturer who replaced the expansion lube oil with a chlorine-based organic solvent, thoroughly cleaned the inside surface of the tube, sealed the tube ends after either a) vacuum drying or b) filling the tube with N₂, and kept moisture away from the tube.

Notoya and Ishikawa (Atrens et al eds, 1989) referred to steam purging of the inside of the tube followed by air drying at 75°C (before sealing the ends) as an alternative to a) or b). Complete success in protecting the inside surface was reported if one of these three steps was followed. Controlling the humidity was mentioned for the protection of the tube outside surface. Protective coatings for the tube outside surface were suggested but without specifics. Notoya (1997a) mentions that polyethylene caps are used to seal the tube ends.

Notoya (1991a, c, d) reported work on inhibitors and vapor deposited metal coatings. Vapor deposited thin layers of Zn, Ni, Ag, Sn, or Pb on copper tubes were tested for thirty days and the exposure was to vapor generated from an aliquot of 0.1% volume formic acid. The micrographs show aggressive attack for all of the cross sections. Nine different inhibitors were applied to two types of copper tubes (phosphorous deoxidized, JIS H3300 (UNS C12200), and oxygen free, JIS H2125 (UNS C10200). The inhibitors tested were:

- 2-Mercaptobenzothiazole (MBT),
- 6-Phenyl-aminotriazine-2,4-dithiol sodium salt (PTD),
- 2-(4-Thiazolyl)-benzimidazole (TBZ),
- 2,5-Dimercaptothiadazole (DMTDA),
- 1-Phenyl-2-thiourea (PTU),
- 2-Mercaptobenzimidazole (MBI),
- 1,2,3-Benzotriazole (BTA),
- 8-Hydroquinoline (HOQ),
- Potassium heptyl-hydroxamate (HOX).

The copper tubes were pickled in a 4-molar solution of chromic acid (CrO_3), rinsed with deionized water, then submerged in a solution of water or methanol with 1% weight of an inhibitor at 60°C for 3-minutes and air dried. The exposures were for thirty-days at room temperature using 1% and 0.1% volumes formic acid which had been saturated with oxygen before the test began. The inhibitors were effective at keeping the tubes free of tarnish (especially the BTA) except at the top end, which developed a green patina. Cross sections showed formicary corrosion under this patina, which Notoya attributes to an end effect. The post-test surfaces on the oxygen free copper were reported to be smoother than those on the phosphorous deoxidized copper.

Later that year (1991e) tests were conducted using the following inhibitors:

- 2-Undecylimidazole (UDI),
- CrO_3 , and
- $\text{K}_2\text{Cr}_2\text{O}_7$

The latter two inhibitors were ineffective but the former treatment allowed the copper tube to resist formicary attack for a forty-day exposure over 0.1% volume formic acid. A 1% volume formic acid solution initiated formicary corrosion pitting after twenty days. The UDI was applied by soaking in a commercial preparation called Glicoat T™ with a pH of 4.35 for up to 60-seconds at 30°C. Notoya attributed the success of the inhibitors to their hydrophobic (literally “water hating” e.g. water repellent) properties and observed that the UDI was more effective than the BTA. Notoya (1991b) suggests the use of more stable detergents and lubricating oils.

In 1992, Notoya and other members of the Corrosion Committee of the JCDA published results of more inhibitor tests (Notoya et al 1992) using:

- 3-Amino-1, 2,4-triazole,
- Dihydropropyl benzotriazole
- and the commercial products:
- Cu Guard™,
- Wondermin 20P™
- Sunbit NaPBT™.

Only the Cu Guard™ was found to be effective; the researchers continued to recommend UDI and BTA. They further recommend that the inside surface of the copper tubes be cleaned before U-joint fittings were brazed. Notoya et al (1995) reported positive results in the treatment with BTA of a beryllium copper coolant system in a supercomputer that had suffered localized attack similar to formicary corrosion.

Miyafuji et al (1995) described testing of various copper alloys in 1% (volume) of formic acid for 10 to 40-days. A Cu alloy with 2% Mn displayed the least depth of formicary attack (less than 0.05-mm) and the fewest number of pits (about three) compared with a number of Cu alloys with smaller amounts of Mn. The authors attribute these results to the Mn ions raising the pH of the potentially corrosive condensate on the copper and the formation of a denser structure of Cu-Mn corrosion products, which slowed the access of the corrosive to the anode surface.

Lenox and Hough (1995) made recommendations for the installation and maintenance of commercial refrigerators and stressed that the copper tubing must be dry and clean before and after installation (some tubes may pick up salts, nitrates, etc., during transport). Adequate ventilation is required to prevent attack from smoke, food vapors, etc., which may concentrate by condensation on the tubes and hydrolyze into carboxylic acids.

In Notoya (1997a) advised that the brazing of a grooved tube to a plain one can create crevices where corrosion can initiate. Care should be taken to flatten the grooves or to fill them with the brazing material. It was further recommended that the tube inside surface be protected using BTA with an inert gas before capping the ends.

Tetley et al (1998) echoed many of the recommendations mentioned above and stressed that the parts be totally dry before brazing to prevent trapping moisture; a “pressure holding rubber plug” is required as a tube cap if the environment is very hot or humid. A coating should be considered if the tube might be exposed to corrosives. A clean manufacturing atmosphere (free from cigarettes and food, not just chemicals) is seen as beneficial.

Kelly et al (2000) stressed that in a commercial cooling system the copper must be clean, the insulation dry, and the vapor barrier 100% effective; the adhesive must be carefully chosen to avoid its breakdown into carboxylic acids.

Notoya (2001a) reported tests with six coatings on phosphorous deoxidized copper (JIS H3300, UNS C12200) exposed to vapors from an aliquot of 1%volume formic acid at room temperature for up to six months. The coatings were:

- black acrylic lacquer 0.035mm thick,
- black baked enamel 0.025mm thick
- gray baked enamel 0.050mm thick
- black epoxy resin (E-Coat™) 0.035mm thick
- off-white epoxy resin 0.180mm thick
- off white polyanilene epoxy resin 0.540mm thick.

The two thickest coatings (the epoxy resins) showed no corrosive attack after six-months.