Fight Formicary Corrosion

By Peter Elliott Corrosion & Materials Consultancy, Inc.

This little understood type of corrosion can quickly pit copper heat-transfer surfaces.

Formicary, or ant's nest, corrosion is a little known phenomenon except to those who have experienced it first hand. It may best be described as micro-pitting in that the surface pits generally are so fine that they cannot be seen by the unaided eye. The first realization of a problem usually comes too late - in the form of a leaking tube.

More instances of formicary corrosion have been recorded during the past ten years than ever before. This reflects investigators' greater awareness of the phenomenon; prior cases probably were blamed on other causes. Attack has been attributed to the growing use of synthetic lubricating oils that were introduced as refrigerant fluids changed some years ago, or to vaporous species derived from the immediate surroundings, including volatiles from process fluids or from woods used in building materials.

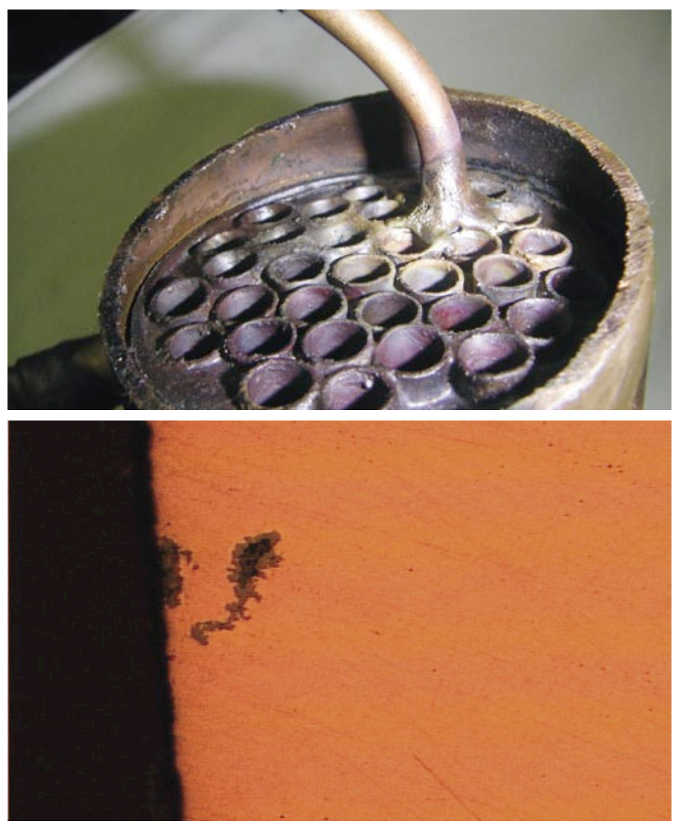
This type of corrosion most commonly appears in copper tubing in air conditioning and refrigeration equipment and has been reported in heat pumps. It, however, also can occur in process equipment, including heat exchangers, coolant piping, freezers, commercial chiller units, water-cooled boilers and fuel-cell heat exchangers.

The time to failure can be as short as weeks, not years. For instance, the 3/16-inch diameter copper refrigerated heat exchanger bundle shown in Figure 1 leaked within weeks; formicary attack was found in similar unused units.[1]

Damage most commonly appears in copper tubing but alloys may also be susceptible to attack. At least one case of formicary corrosion has been reported in a commercial heat exchanger made with cupronickel tubes. Selected metallurgical sections do not always show complete penetration because formicary "tunnels" are so fine that they may be ground away in preparing the section. There are no reported cases of formicary attack in other metals.

Damage typically is found in shielded areas (crevices) in closed heat exchanger bundles or between copper tubing and aluminum fins in heating/ventilation/air- conditioning (HVAC) systems. Formicary corrosion occurs when

Figure 1. Formicary corrosion occurred within eight weeks of service, with localized micro-pitting "tunnels" advancing into the copper tubing (unetched section, 500X magnification).



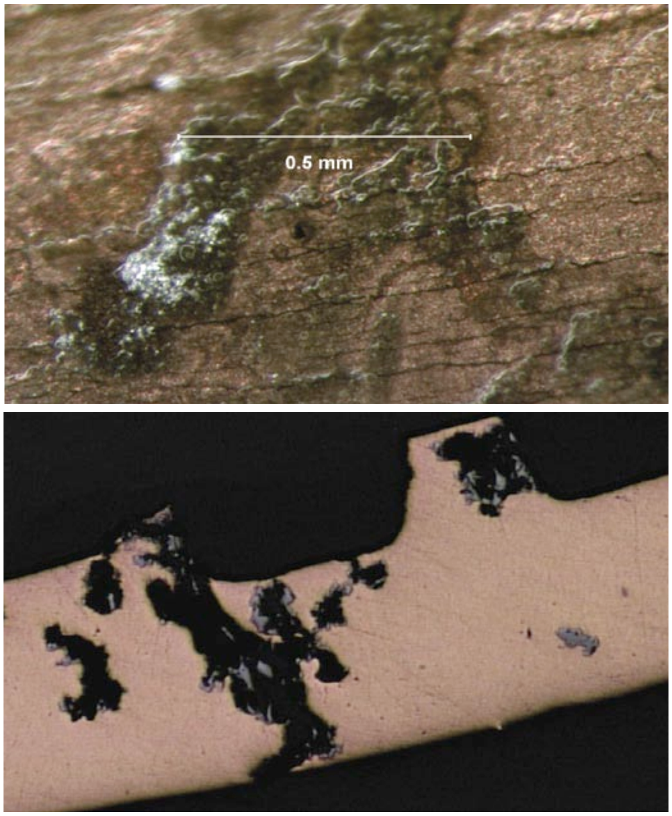
air, moisture and certain organic compounds are present, with crevices the most likely sites for attack to initiate and propagate. Crevices favor corrosion processes because attack probably is exacerbated by differences in oxygen concentration (differential aeration). Access to evaluate attack generally is hindered by the heat exchanger or coil geometry; helium-sensing devices are useful to locate pinhole leaks.

Formicary pits in copper are miniscule as shown in Figure 2a compared with those caused by aqueous solutions containing chlorides. The latter pits are easy to see and may show copper corrosion products. By contrast, the copper surface adjacent to a formicary pit typically is discolored with surface films of various hues from purple/red-brown to dark gray.[1-3]

The Sources

Formicary corrosion pits form when certain residual organic compounds degrade in the presence of air and moisture to produce carboxylic acids such as formic and acetic acid. Chemical sources of formicary corrosion include chlorinated organic compounds (trichloroethane, trichloroethylene, etc.) or hydrolysis products from the decomposition of, for example, esters or aldehydes and alcohols. Sources of corrodent include synthetic lubricating oils used for forming and joining copper tubes, degreasers and detergent cleaners, inhibited antifreeze solutions, brazing or soldering fluxes, volatile substances from building materials (e.g., in woods used in roof spaces subject to seasonal high humidity), foods and food processing (such as vinegar, vegetable oil dressings and liquid smoke), certain adhesives and some insulation barriers.

Figure 2. Copper tubing exhibits (a) surface pit on its inside diameter and (b) through-wall formicary "tunnels" (125X magnification).



Attack starts at some local discontinuity on the metal surface, such as a defect or small scratch in the surface oxide or metal; the process continues as a self-propagating randomly distributed pattern of "tunnels" that may ultimately penetrate through the metal section as shown in Figure 2b. The term "ant's nest corrosion" stems from the similarity of the morphology to an ant's nest.

It generally is agreed that formicary corrosion requires the presence of a low-molecular-weight organic compound, as well as air and moisture. Removing any of these should eliminate the problem.

Stagnant shielded conditions such as crevices in assembled coils favor the onset of formicary corrosion. Clean and dry surfaces will be free from formicary attack; local stresses in the metal and grain size may contribute to attack.

The role, if any, of bacterial corrosion in formicary attack is not clear. In general, micro-organisms do not grow prolifically on copper. However, some organisms in stagnant conditions can oxidize carbon sources to carbon dioxide and water to obtain energy through a tricarboxylic acid cycle that produces carbon compounds. If the tricarboxylic acid cycle is not completed, organic acids (predominantly citric acid) are released into the environment. It is not known if these acids contribute to formicary corrosion.

Control Measures

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Formicary corrosion attack increases at higher temperatures, especially if the corrodent source (organic compound) is thermally degraded to yield a carboxylic species. In laboratory tests, suspect fluids generally are hydrolyzed (refluxed at about 105 °C for 48 hours) before aqueous extracts are analyzed for carboxylic species.[4] Selecting substances with low carboxylic content (typically below about 20 mg/L for the as-hydrolyzed products) should minimize or eliminate the problem in service. For more confidence in the anticipated service performance, conduct additional long-time (up to three months) testing of the copper tube with vapors of the candidate fluid or substances that are present on the surfaces of the subject component, with metallurgical evaluation of the metal section after testing.

Despite better understanding of formicary corrosion, effective and economic cures are still lacking. Research that started in Japan[3] has continued to gain momentum worldwide as the phenomenon has garnered more recognition. The most recent comprehensive study, directed towards a screening test for formicary corrosion, was supported by the Air Conditioning and Refrigeration Technology Institute.[4] Palliative measures under consideration include the use of lubricating fluids with lower carboxylic content, hydrophobic coatings that reduce the effects of humidity and more-corrosion- resistant alloys.

Success in dealing with formicary attack, like many other forms of corrosion, depends upon awareness - with control, rather than elimination, the realistic goal.

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