

Formicary Corrosion and EAC of Copper Tubes in Contact with Building Sealant

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ABSTRACT

Copper tubes for carrying medical-grade gasses were installed during construction in multiple medical facilities. Where the tubes penetrated drywall separating individual rooms, the perimeter surfaces of the tubes were sealed with building sealant to suppress noise, smoke, and fire transmission. During construction, discoloration of the copper tube where sealant had been applied was observed. A laboratory investigation determined the observed discoloration was copper corrosion product. Further laboratory evaluation of the system was performed to characterize the discoloration, the underlying copper tubes, and sealant using a variety of techniques. Evaluation of the copper tubes indicated nitrogen-containing deposits on the outside diameter (OD) surface as well as features consistent with formicary corrosion and environmentally assisted cracking (EAC). While through wall-cracking or corrosion had not occurred, the investigation indicated that failures were possible if the discolored pipes were placed into service as constructed. Evaluation of the sealant indicated it contained nitrogen-containing compounds and formic acid. Certain nitrogen-containing compounds are associated with EAC of copper, and formic acid is associated with formicary corrosion of copper. The results of the investigation determined that the sealant was not compatible with the copper tubes.

Key words: corrosion mechanisms, stress corrosion cracking, materials performance, corrosion science and technology, reactions (chemical)

INTRODUCTION

Blue discoloration of off-white sealant in contact with copper tube at medical facilities under construction was observed. The copper tube was being installed to transport medical-grade gasses and the sealant was used as an acoustical and smoke sealant at through-wall penetrations. In some areas of one facility, galvanized steel pipes inserts were used as sleeves for the copper pipes through the drywall, while in other areas, the copper pipe penetrated directly through the drywall. Observations of the discoloration prompted an evaluation of the copper tube, sealant, and potential adverse interactions.

Laboratory evaluation of samples removed from the buildings was performed to evaluate potential interactions of sealant with copper, evaluate the condition of the copper tubes, and the composition of

the sealant. Testing indicated that the discoloration occurred as a result of chemical interaction of the copper with uncured sealant applied from the tube. Furthermore, the sealant led to discoloration of the copper and buildup of corrosion products which was greater if the copper tube was sealed inside a galvanized steel pipe insert. Microscopic evaluation of the copper tubes in contact with the sealant indicated features associated with formicary corrosion and environmentally assisted cracking (EAC). Chemical analysis of the sealant indicated the presence of water-soluble formic and acetic acid salts, and their conjugate acids, which are known to cause formicary corrosion of copper. Additionally, water-soluble ammonium (in some samples) and possible amines, which, along with acetic and formic acids, are associated with EAC. As a result of the evaluation, the copper tubes were recommended to be removed and replaced prior to building completion.

EXPERIMENTAL PROCEDURE

Samples

Several samples of copper tube with intact through-wall penetration assemblies were received. The copper tubes were UNS C12200, compliant with ASTM⁽¹⁾ B819¹, suitable for use with medical grade gasses. Sample A is shown in Figure 1 and consisted of a copper tube sealed to a galvanized tube sleeve which is sealed to drywall. Samples B – G consist of copper tube penetrating drywall and sealed to the drywall. A photograph of Sample B, showing the penetration of the copper tube through the drywall, is shown in Figure 2. In addition to the tube samples, unused containers of sealant representing different lots of the material used on these projects was supplied for laboratory study.



Figure 1: Sample A as received.

¹ ASTM International, 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959.

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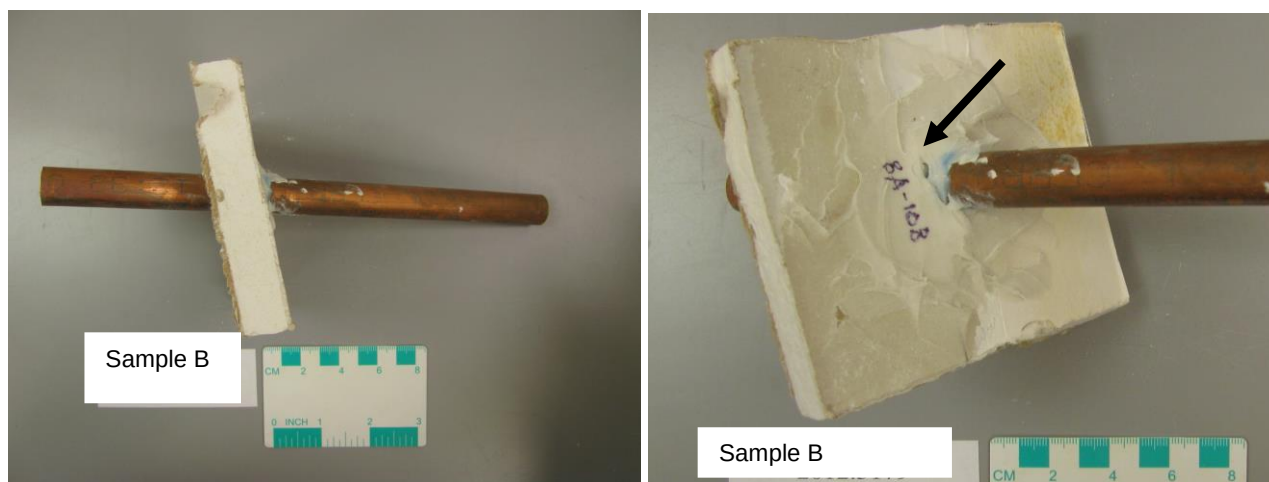


Figure 2: Sample B as received, showing the tube penetration through the drywall on the left, and the sealant at the tube location on the right. Note the blue discoloration of the tube, indicated with an arrow in the photograph on the right.

Visual Observation and Microscopical Examination of Copper Tubes

Copper tubes were removed from the building with sealant seams intact; a portion of the drywall and galvanized steel pipe were included, if present, and delivered to the laboratory intact. These samples were examined visually and specimens collected for microscopical examination. Specimens were examined both as-received and after cross-sectioning. Microscopy was conducted using a Nikon SMZ 800[†] stereomicroscope, a Zeiss ICM 405[†] inverted reflected light microscope, and JEOL 6010LA[†] scanning electron microscope with energy dispersive x-ray spectrometer operated at 20 kV.

Chemical Analysis of Deposits on Copper

Deposits on copper tubes were analyzed using Fourier transform infrared spectroscopy (FTIR) using a Perkin Elmer Spectrum 100[†] spectrometer with an attenuated total reflectance (ATR) accessory and by x-ray diffraction (XRD). XRD analyses were conducted on a Bruker D8 Advance[†] diffractometer using copper K α radiation.

Chemical Analysis of Sealant

Sealant samples removed from the tubes as well as laboratory-cast samples of reference sealant were analyzed using FTIR-ATR using the same instrument and technique as the deposits on the copper tube. Additionally, the chloroform-soluble components of the sealant were analyzed using transmission FTIR analysis. Discolored sealant was analyzed for elemental composition using SEM/EDS.

Water-soluble ionic concentrations of the sealant were determined by analyzing water extracts with ion chromatography (IC). Extraction consisted of placing a defined amount of sealant, cut into pieces into a plastic bottle with deionized water at a 10 mL/g ratio. The bottles were capped, placed in a water bath at 45°C for 24 hours and the extract filtered and analyzed. IC was performed using a Dionex ICS 2000[†] ion chromatograph with a conductivity detector and hydroxide eluent, a Dionex AS 15[†] column for anion analyses and methanesulfonic acid eluent and a Dionex CS 17[†] column for cation analyses. Standards of fluoride, formate, acetate, chloride, bromide, nitrite, nitrate, sulfate, bromide, phosphate, lithium, sodium, potassium, ammonium, magnesium, calcium and triethanolamine were used for quantification.

[†] Trade name.

Exposure Tests of Sealant and Copper

Exposure tests of uncured sealant and Type L copper tubes were performed by applying sealant directly from the container to the cleaned copper tube. Some samples were placed in a closed container to retard evaporation of volatile components of the sealant and mimic the condition with the galvanized tube sleeve, while other samples were left to cure in the laboratory environment to mimic the condition where sealant was placed at the copper tube/drywall interface.

RESULTS

Visual Observation and Microscopical Examination of Copper Tubes

Sample A

The through-wall penetration assembly of Sample A was examined visually as received. The galvanized steel pipe and copper tube did not appear to be in direct electrical contact at any point. The portions of the copper tube on the exterior of the drywall had a slightly dull copper color that is typical of copper that has been exposed to an air environment. In the immediate vicinity of the sealant, the copper tube was blue in color (Figure 3). The sealant was also blue at contact surfaces with the copper pipe. The sealant in contact with the galvanized steel pipe was generally not discolored.



Figure 3: Sample A, showing discoloration of sealant and copper at contact location (left) and shiny copper when sealant was removed (right).

The galvanized steel pipe sleeve was removed. Significant amounts of deposits and discoloration were apparent on the surface of the copper tube (Figure 4). The deposits were observed to consist of four apparent colors and morphologies. Smooth green discoloration, smooth dark blue discoloration, and a small amount of dark blue/green liquid were also apparent, along with purple to transparent crystals (Figure 5). Samples of each type of deposit were collected for further analysis.