

EVALUATION OF THE TENDENCY TOWARDS FORMICARY TYPE CORROSION OF COPPER TUBES IN THE HEAT EXCHANGERS FOR AIR CONDITIONING

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ABSTRACT: A specific type of corrosion named formicary corrosion or "ant nest corrosion" has been reported in copper tubing of evaporator type heat exchangers used for residential air conditioning, before shipment or shortly after installation. The failure consists in a corrosion penetration of the wall of the copper tubing that results in leakage of the refrigerant. The formicary corrosion phenomenon is not fully understood yet and does not exist a clear solution to eliminate this corrosion problem. It is generally believed that this corrosion type is caused by one of two factors: the decomposition products of processing fluids left on the heat exchangers during manufacture or corrosive materials in the air stream of the space being conditioned. In this paper, condensed water from corroded heat exchangers was analyzed and the tendency of the materials to hydrolyze and produce carboxylic acids was evaluated. Also, most commonly used oils were investigated in a fast experimental set-up in order to evaluate their influence on formicary corrosion of heat exchanger components. Based on these investigations, two oil types for the manufacturing of copper tubes and another two oil types for the manufacturing of aluminum fins were selected.

KEYWORDS: Formicary corrosion, copper tubing, heat exchangers.

1. INTRODUCTION

Many heat exchanger (HX) manufacturers in Japan and USA have received reports of leakage in evaporator coils [1-3]. These HX have copper tubes and aluminum fins [2]. Most leaks were found in copper tubes in the fins pack region. Suspected cause was a specific corrosion type named formicary corrosion or "ant nest corrosion", which is a peculiar form of pitting corrosion [1,4]. This corrosion type is characterized by microscopic caverns connected by tunnels and contains porous copper oxide. Only marks of a brownish red or reddish brown color might be recognizable around the pits, and no greenish blue corrosion products cover the pits as in common pitting corrosion of inner surfaces of Cu tubing [1]. In fact, formicary corrosion phenomenon is not fully understood yet and a clear solution to eliminate it has not been found. Therefore, the air conditioning industry is seriously affected by this problem which became evident in early 1980's [5]. Investigations on formicary corrosion showed that the phenomenon is most severe on the outer surface of the copper tubes. Interesting fact is that as the residues in copper were reduced, the formicary corrosion became more intense.

In 1988 the Corrosion Committee of Japan Copper Development Association stated that formicary corrosion was successfully reproduced in laboratory [6]. It was found that by increasing the concentration of formic acid from 0.01 to 10 vol. %, corrosion becomes severe. Furthermore, a

temperature increase or cyclic conditions plus oxygen and water are considered to promote formicary corrosion [6]. Phosphorous deoxidized and de-sulphurized copper tube (not oxygen free copper) and also, borofluoride flux used for Cu pipe soldering were suspected to favor formicary corrosion. Specific environment chemicals, such as, chlorinated hydrocarbon (especially 1.1.1-trichlorethane base) or coexistence of chlorinated hydrocarbon and water [6,7] were also blamed for formicary type corrosion. In addition, phosphoric inhibitors added to circulating water, sulfide yielded from decaying S compound from S added rubber, HF (and other fluoride compounds), formaldehyde from aldehyde [1], trimethylene (a {phosphoric acid-anticorrosive} which was added to cold/hot water) [3], a certain carbon film and chemicals in alkaline water (pH 7.3-7.9) such as PO_4^{3-} , SO_4 , HCO_3 and Cl are suspected to form formicary corrosion. Some oils or specific chemical components present in oils are suspected to produce formicary type corrosion. These oils are used as lubricants during bending of hairpin tubes and pressing of fins. For example, Polyalkyleneglycol (a lubricant) containing water is easily decomposed into formic acid known as an agent that causes formicary corrosion [7]. Also, formic acid can be generated through the hydrolysis of the alcohol, ester or ether that is added to the lubricating oil to improve its oiliness [3]. Oil inhibitors such as a trimethylene phosphoric acid is also related with the occurrence of the pitting corrosion [3]. When used properly, inhibitors can curb the anodic and cathodic processes, thus reducing the corrosion rate. On the other hand, misuse of an inhibitor can, in fact, accelerate corrosion [8]. In addition, formicary corrosion was linked to weak carboxylic acids, such as formic acid and acetic acid created through the decomposition of lubricating oils [3].

The results published so far indicate that formicary corrosion can be induced by the contaminants interacting with water on the surface of heat exchanger components or by the decomposition of oils in water which can lead to the formation of acid radicals. Because we can not control the environment it will be reasonable to protect copper from destructive chemical interaction. This result can be obtained by using corrosion inhibitors in oil(s) interacting with copper and also by increasing the adherence of such oil(s) to the copper surface. Also, it is important to select proper volatile lubricating oils to prevent formicary corrosion. This paper presents two type of investigations: investigations on corroded copper tubes in order to assess the possible causes of failure and investigations of oils used as lubricants during HX manufacturing in order to evaluate their suitability.

2. EXPERIMENTAL INVESTIGATIONS

The first step was to investigate the coils returned to the manufacturer. These investigations indicate that the leaks were caused by outside corrosion of the copper tube. Leaks were found in the center of the coil, in the fin pack and at the tube bends (see Figure 1). Samples of copper tubing from corroded coils were also prepared for hardness measurements (H_K 0.5). Results indicated an increase of hardness by 39% for corroded samples relative to non-corroded samples. This increase in hardness can be attributed to the copper oxide found in the corrosion pits. Data obtained by energy dispersion spectroscopy (EDS) from pits localized on the outer surface of the copper tube for two samples are shown in Table 1. One interesting fact is that, inside the corroded region, both samples contain high level of Al. The presence of Al on corroded area can be the result of a chemical reaction between the Cu tube and Al fin. These observations confirm the presence of formicary corrosion. The pits forming beneath the

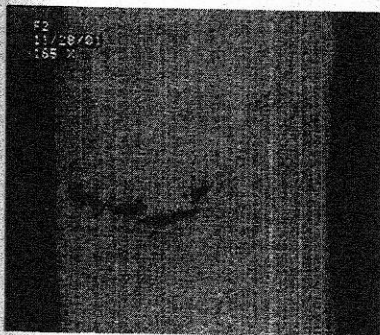


Figure 1. Example of formicary type corrosion of a copper tube in the bending zone.

aluminum cooling fins due to chloride and/or sulfate attack was the suspected cause. It is also possible that chlorine, fluorine or bromine atoms from the refrigerant halogen-bearing gas can be deposited on the corrosion area after the leak developed in the copper tube. Another possibility is the dissolution of copper from the coil wall followed by its migration to other areas within the system and deposition on metals of lower electrochemical potential (such as aluminum) which accelerate corrosion.

During field investigation condensed water was collected from the regions affected by this type of external corrosion failure. In most cases, high concentrations of formic acid, acetic acid and chloride were found in condensed water drop out from the evaporator coil (see Table 2).

Table 1. EDS data from pits situated on the outer tube surface for two samples.

Element	O %	Al %	Cu %	Si %	S %	Cl %	K %	Ca %	Fe %
Sample 1	49.35	21.53	18.12	3.84	1.87	1.76	0.96	0.63	1.93
Sample 2	45.71	18.54	25.95	2.22	1.82	2.84	1.24	0.58	0.95

Table 2. Matrix on condensed water investigation from the evaporator coils field failures.

Sample No.	1	2	3	4	5	6	7
Acetic Acid (mg/l)	62	56	-	-	-	23.2	81
Formic Acid (mg/l)	-	-	-	-	-	11.6	25.5
pH	5.5	4.9	6.1	4.8	5.1	4.9	4.6
Nitrate-N as H (mg/l)	-	0.2	-	0.2	0.2	-	0.2
Phosphorus	-	-	-	0.118	0.367	-	-
Chloride (mg/l)	-	1.3	1.5	-	-	1.1	1.3

To select a proper lubricant to be used for the heat exchangers production, a number of ten past, present and possible future production oils were investigated. Hydrolysis investigations for oils were performed by an independent laboratory (ATS, Inc in Marietta, GA) aiming to quantify the concentration of formic and acetic acids as well as the drop in pH value at the end of the test (see Table 3). No significant drop in pH value and low levels of formic and acetic acids after hydrolysis test was considered to be a good factor for oils selection. Data shown in Table 3 indicate that OAK 11B from Oak Co. and TL-XG-99B from CFB Inc. are the best oils for copper hairpin tube bending and expansion. Also, Arrow 5894FR, an evaporative lubricant for Al fins from Chem Arrow Corporation International, and AF 12M60 are suitable oils for the aluminum fins press.

Copper alloys containing 1% Mg, (designed to be resistant to formicary corrosion) have recently been developed, but these alloys are expensive and the benefit need to be validated by field investigations. Also, coating of the external coil surface has also been proposed as a solution [9] but it implies an extra process and will increase the final production cost. A viable inexpensive solution can be the introduction of corrosion inhibitors in the oils used as lubricants in the production of copper tube and aluminum fins that will not have negative effect on heat transfer. Based on this simple idea an accelerated formicary corrosion test was developed to test and select oils used in manufacturing of evaporators.

3. ACCELERATED CORROSION TEST

The effect of diverse oil decomposition products on the HX was analyzed using a fast experimental set-up. Nine test vessels were filled with 100ml acid solution. This solution was 1% formic acid (90% purity) and 5% commercial grade vinegar by volume in deionized water. Test vessels were 1000ml air/oxygen tight glass containers sealed with provided lid. Samples inside glass vessels were cycled between 40 °F to 230 °F for forty complete cycles using a Thermotron S 12

Environmental Chamber for 72 hours. With this experimental set-up, 8 oil combinations for copper tube and 8 oils combinations for aluminum fins used in HX were tested. Based on the test results, oil types for copper tube and for aluminum fins were selected. Samples marked with arabic numbers are samples of copper tube or aluminum fins tested alone. Samples marked with roman numbers are samples of copper tube or aluminum fins tested together.

Table 3. Matrix for oils used during coil's fabrication. (*new, suggested oils)

Oil Type	General Information	Corrosion fast test	Hydrolysis (ppm) formic/ acetic acid	pH change during hydrolysis	Used for
OAK 11B	Petroleum, hydrocarbons, expensive		0.3/1 old 0.6/1new	6.8-7.6old 6.7-5.8new	Hairpin bending & expansion
OAK 11E	Petroleum, hydrocarbons, high viscous, less expensive		4.5/5.5 new	6.7-4.2 new	Hairpin bending & expansion
OAK 15CT	Petroleum, hydrocarbons (polymeric-based), low viscous	Strong visual degradation	32/28	6.7 - 4.5	Hairpin bending & expansion
Arrow 4992 Penetrating Lubricant	Petroleum, hydrocarbons, solvent with lubricity additives		33/27	6.8 - 3.4	Galvanized steel cabinets
Arrow 894FR Vaporative Lubricant	Petroleum hydrocarbons (mixture of hydrocarbons with ester of adipic acid)	Strong to moderate visual degradation with Oak 15CT	4/1	6.7 - 7.6	Al fin press
TL-NXG™ 99B CPB Inc.	Petroleum, hydrocarbon with corrosion inhibitors	OK with Arrow 8997FR		6.7 - 6.7	Hairpin bending & expansion
TL-NXG™ 99 CPB Inc.	Petroleum, hydrocarbon with corrosion inhibitors	OK in combination with AF-12M60	2.1/3.8	6.8 - 5.2	Hairpin bending & expansion
AF-12M60 CPB Inc.	Water base with 0% VOC and corrosion inhibitors	OK in with TL-NXG-99	Can't be measured using IC	6.8 - 7.7	Al fin press
TL-44AX CPB Inc.	Isoparaffinic, hydrocarbon		7.2/2.1	6.8 - 5.0	Al fin press
III-50 Murakawa	For grooved copper tube		135/40	6.8 - 3.4	Copper drawing
Arrow 4595	Aliphatic polymer based with corrosion inhibitors	Visual improvement	27/26	6.8 - 3.9	Hairpin bending & expansion
Arrow 894FR Vaporative Lubricant Low VOC	Petroleum solvent with lubricity additives 60% VOC	Moderate visual degradation with Oak 15CT OK with TL-NXG-99B	31/47	6.8 - 3.5	Al fin press

Table 4. Tested oils combinations.

Type & #	OAK11 B	TL-NXG99	AF-12M60	FL-44 AX	ARROW 8997FR	ARROW 5894FR	Oak 15CT	TL-NXG99B	Average corrosion pit size (mm)
Cu-1	X								
Cu-2		X							
Cu-3		X	X						0.03-0.04
Cu-4		X		X					
Cu-5	X					X			
Cu-6	X		X						
Cu-7		X				X			
Cu-8	X			X					
Cu-9						X	X		0.85
Cu-10	X					X			0.55-0.65
Cu-I						X		X	0.55
Cu-II					X			X	0.05-0.22
Cu-III		X	X						0.03-0.05
Cu-IV		X		X					0.03-0.35
Cu-V								X	0.05
Cu-VI	X					X			0.75
Cu-VII	X				X				0.5
Cu-VIII						X	X		>1
Cu-IX			X		X			X	0.03
Al-3		X	X						0.05
Al-4		X		X					
Al-5	X					X			
Al-6	X		X						
Al-7		X				X			
Al-9						X	X		0.05
Al-10	X					X			0.1
Al-I						X		X	
Al-II					X			X	
Al-III			X					X	
Al-IV				X				X	
Al-V								X	
Al-VI	X					X			
Al-VII	X				X				
Al-VIII						X	X		

4. TEST RESULTS

With only two exceptions (see #3 and #I II samples in Table 4), all of the oil combinations tested did not perform acceptable on grooved copper tube for this corrosion test. Exist solely as a minimum visual degradation difference on the grooved copper samples coated with OAK 15CT (see # 9) relative to the same copper grooved tube samples coated with OAK 11-B (see #10). The copper tube sample coated with OAK 11B (see # VII) performs slightly better relative to the sample coated with OAK 15CT (see # VIII). Only the combination of oils such as TL-NXG-99 with AF-12M60 (see # 3) and TL-NXG-99B with ARROW 8997FR (see # II) perform satisfactory (not discernible corrosion pits) for the copper tubes used during this accelerated corrosion test.

5. CONCLUSIONS

Considering these results it is recommended for production to use the TL-NXG-99 oil for copper hairpin bending and expansion and the AF-12M60 for aluminum fin press. As an alternative or temporary solution TL-NXG-99B oil for copper hairpin bending and expansion and the ARROW 8997FR for aluminum fin press can be used (see Table # 3).

Also, it was recommended to the manufacturer to improve HX quality by removing any contaminants such as organic detergents and lubricant oils by steam cleaning and drying with hot air. Also, it is desirable to design a heat exchanger without any crevices. When a plain tube is brazed to a grooved tube, the grooves should either be flattened before brazing or filled with a brazing filler metal to avoid the occurrence of micro-crevices.

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