



Title	Localized Corrosion in Copper Tubes and Its Inhibition by Surface Pretreatment with 2-Undecylimidazole
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Citation	Memoirs of the Faculty of Engineering, Hokkaido University, 18(2), 15-21
Issue Date	1991
Doc URL	http://hdl.handle.net/2115/38042
Type	bulletin (article)
File Information	18(2)_15-22.pdf



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Localized Corrosion in Copper Tubes and Its Inhibition by Surface Pretreatment with 2-Undecylimidazole

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(Received August 30, 1991)

ABSTRACT

Localized corrosion protection in copper tubes was evaluated in an exposure test. This particular method can be achieved by pretreating the copper tubes with four different inhibitor solutions. The untreated and pretreated copper tubes were exposed to a humid atmosphere over an acid solution containing a small amount of carboxylic acid (such as formic acid, acetic acid or propionic acid) in an airtight glass vessel for 40 days. 2-Undecylimidazole showed excellent performance and proved superior to benzotriazole. Pretreatment with chromic acid and potassium dichromate hardly any protection against localized corrosion in copper tubes. Optical micrographs showing cross sections of the localized corrosion with and without these inhibitor pretreatments are presented.

1. Introduction

Copper tubes are widely used in refrigerating and air-conditioning units. Corrosion in such copper tubing generally takes the form of uniform tarnishing, pitting, stress corrosion cracking and corrosion fatigue. A further form of copper tube corrosion has been detected early in use and even during leakage tests after manufacturing. The morphology of this corrosion is similar to an "ant-nest" when viewed in cross section. The pinholes penetrating the copper walls are generally difficult to detect by the naked eye. However, when observed with an optical microscope it can be seen that cross sections of corroded parts are characterized by the development of an underlying labyrinth of interconnecting channels which contain porous copper oxide (Cu_2O) in directional pits.

This type of corrosion was first noted in the early 1970s when one case was reported by Edwards et al.⁽¹⁾ in Canada. The corroded copper pipes were used for cooling water in an air-conditioning system. Leaks from numerous pinholes were detected during pressure tests after installation, but no mechanism for the corrosion was clarified. Yamauchi et al.⁽²⁾ reported over 20 cases of such corrosion in Japan before 1984 and found that all cases occurred in copper tubes in air-conditioning units. Most instances were detected early in service or during pressure tests at the time of installation. This corrosion may have occurred while the equipment was being assembled. It was suggested that the corrosion was promoted by decomposition products from chlorinated organic solvents used to degrease the tubes. Laboratory tests suggested that this kind of corrosion could be produced by water with hydrochloric acid and phosgene

(COCl₂), which are formed by the hydrolysis of 1. 1. 1-trichloroethane.⁽²⁾

Notoya has reported 64 cases of premature failure of copper tubes over 11 years from 1978 to 1988.⁽³⁾⁽⁴⁾ That report details the date of detection, the application of the copper tube, time of failure, the wall thickness and possible corrosives. The copper tubes used were predominantly phosphorus deoxidized copper. This localized ant-nest corrosion can be simulated in vitro in a humid atmosphere in the presence of a small amount of carboxylic acid.⁽⁴⁾⁽⁵⁾⁽⁷⁾ It is believed that the corrosion is caused by this small amount of carboxylic acid, produced by the hydrolysis of chlorohydrocarbons, such as 1. 1. 1-trichloroethane which is used as a detergent.

Recently it was reported in the United States that ant-nest corrosion occurred in Japanese-made copper tubes and other foreign-made copper tubes in air-conditioning units. In all of these cases, self-evaporating lubricant oil, OAK A, was used during the hairpin bending process and chlorohydrocarbon (such as 1. 1. 1-trichloroethane) was not used during the process of degreasing. A simulated test using self-evaporating lubricant oil proved that the ant-nest corrosion was again caused by carboxylic acids resulting from the hydrolysis of self-evaporating lubricants.

Efforts have been made to prevent such localized corrosion in copper tubes and some of the preventive measures will be proposed in this report. ie, the type of corrosion initiated at the inner surface of copper tubing can be prevented by modifying the manufacturing processes for air-conditioners.⁽⁵⁾ The conventional manufacturing process consists of five steps: (i) Mechanical expansion of copper tubes to attach aluminum fins is carried out, (ii) The use of organic solvent to degrease the inner surfaces of the tubes, (iii) Brazing U-bent tube fittings at 730° to 780°, (iv) Pneumatic leakage tests at 28 kgf/cm², and (v) Treatment of the inner surfaces.

The treatment of the inner surface of the copper tubes should be conducted by one of the following methods; (i) Hot air drying at 75°C, after the steam cleaning, to remove organic detergents and lubricants which are left over in the copper tubes, (ii) Sealing the tube ends after vacuum drying, or (iii) Sealing the ends after filling the tubes with nitrogen. No corrosion initiated at the inner surface has been found after taking these preventive measures, and they are considered to be fully effective.

It is believed that corrosion initiated at the outer surface can also be prevented by correct humidity control of the immediate environment and by applying protective coatings. This report presents an alternative method of inhibiting ant-nest corrosion: by surface pretreatment of copper tubes with 2-undecylimidazole. Test results were compared with the corrosion in untreated copper tubing as well as with those pretreated with chromates and benzotriazole.⁽⁶⁾

2. Experimental

Exposure tests were performed to evaluate the anti-tarnishing surface treatment, using two different kinds of copper tubes: 50 mm in length, 6 mm in diameter and 0.5 mm thick-walled phosphorus deoxidized copper tube (PD copper, JIS H3300; Cu 99.9 and P 0.015-0.040) and 50 mm in length, 6 mm in diameter, 1 mm thick-walled oxygen free high-purity copper tube (OF copper, JIS H2125; Cu 99.99, Fe 0.0005, As, Sb, Sn 0.0002, Si, Bi, Ni 0.0001, Pb 0.0003, Ag 0.0007, O₂ 0.0003 and P 0.0004). The method

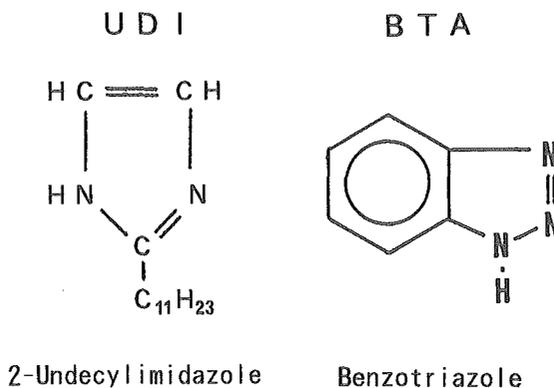


Figure 1 Chemical structure of inhibitors

used is very typical of anti-tarnishing treatment for copper products.

(1) *2-Undecylimidazole treatment*

As-received copper tubes were immersed in a Glicoat T (2-Undecylimidazole solution of pH 4.35), which contains an ionized 2-undecylimidazole, at 30°C for 10, 30 and 60 sec. This was followed by rinsing in distilled water to remove the unreacted inhibitor, and finally, dried in air. The Glicoat T solution was supplied by Shikoku Chemical Co, Ltd. Glicoat T-treated copper surface shows soft-gloss interference color. An ionized undecylimidazole in the Glicoat T solution displays high chemical reactivity with copper. Together, they form a Cu-complex monomolecular layer on the surface of the tube. The undecylimidazole molecules then pile up in layers on the monomolecular layer with the van der Waals force between the long chain alkyl groups.⁽⁸⁾ The film thus formed exhibits a highly hydrophobic nature due to the long-chain alkyl groups, and is considered to act as an anti-corrosive barrier film which prevents moisture accumulation on the surface, hence tarnishing.

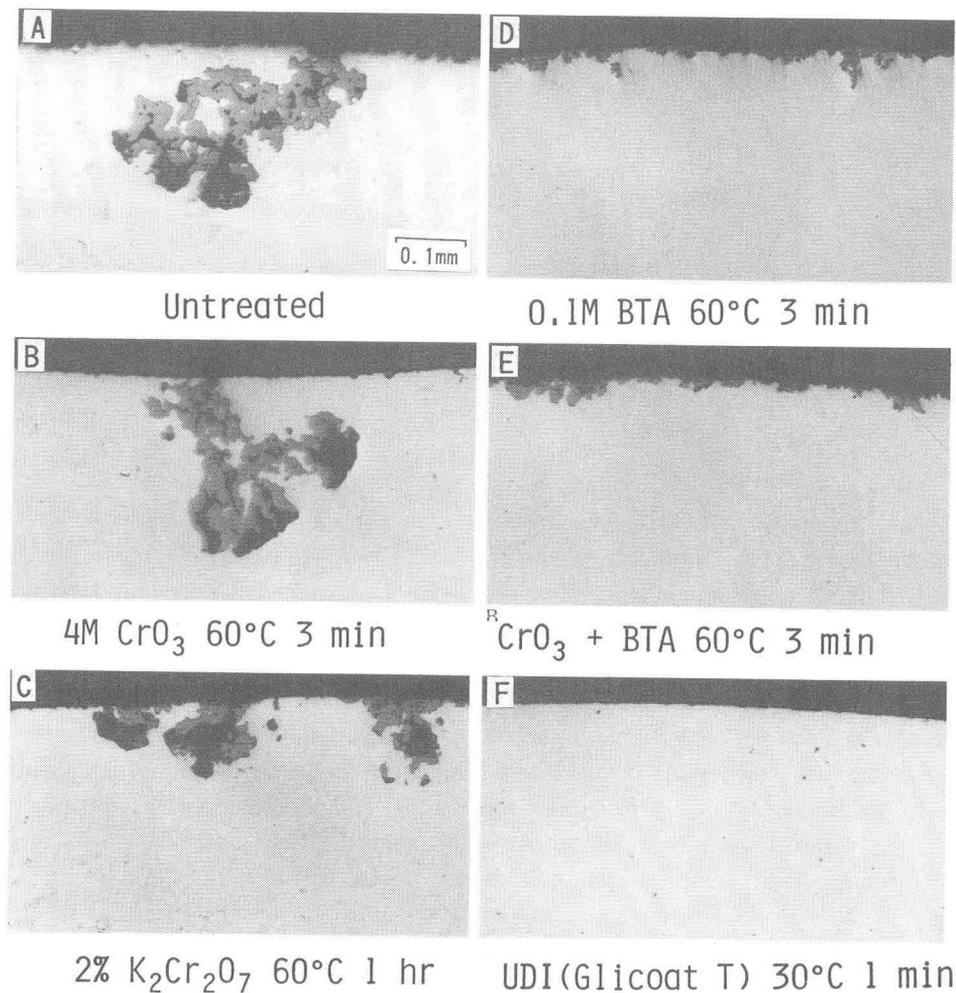
(2) *Benzotriazole treatment*

As-received copper tubes were immersed in 0.1 M benzotriazole (BTA) solution at 60 °C for 3 min, and then rinsed in distilled water, and finally dried in air. During the treatment of the copper tubes with BTA solution, a polymeric structure of Cu^(II)-benzotriazolate (CuBTA) film is formed on top of Cu₂O interlayers on the copper surface.⁽³⁾⁽⁹⁾ This multilayer film (less than 60 Å), which is composed of Cu/Cu₂O/CuBTA, usually gives considerable protection even in a wet atmosphere.⁽¹⁰⁾ The chemical structure of 2-undecylimidazole and benzotriazole is shown in Figure 1.

(3) *Chromic acid and Potassium dichromate treatments*

Copper tubes were immersed in 4 M chromic acid solution at 60 °C for 3 min, or 2% potassium dichromate solution at 60 °C for 1 hr, and rinsed with distilled water, then dried in air.

These pretreated and untreated PD and OF copper tubes were then placed in a humid atmosphere of over 1 liter of water containing 0.1 and 1 vol % formic acid, acetic acid or propionic acid in an air-tight 7 liter glass vessel at room temperature. The experiment was conducted over a continuous period for up to 100 days.



Cross-section of phosphorus deoxidized copper tubes after 40 days exposure to a humid air over 0.1 vol % formic acid.

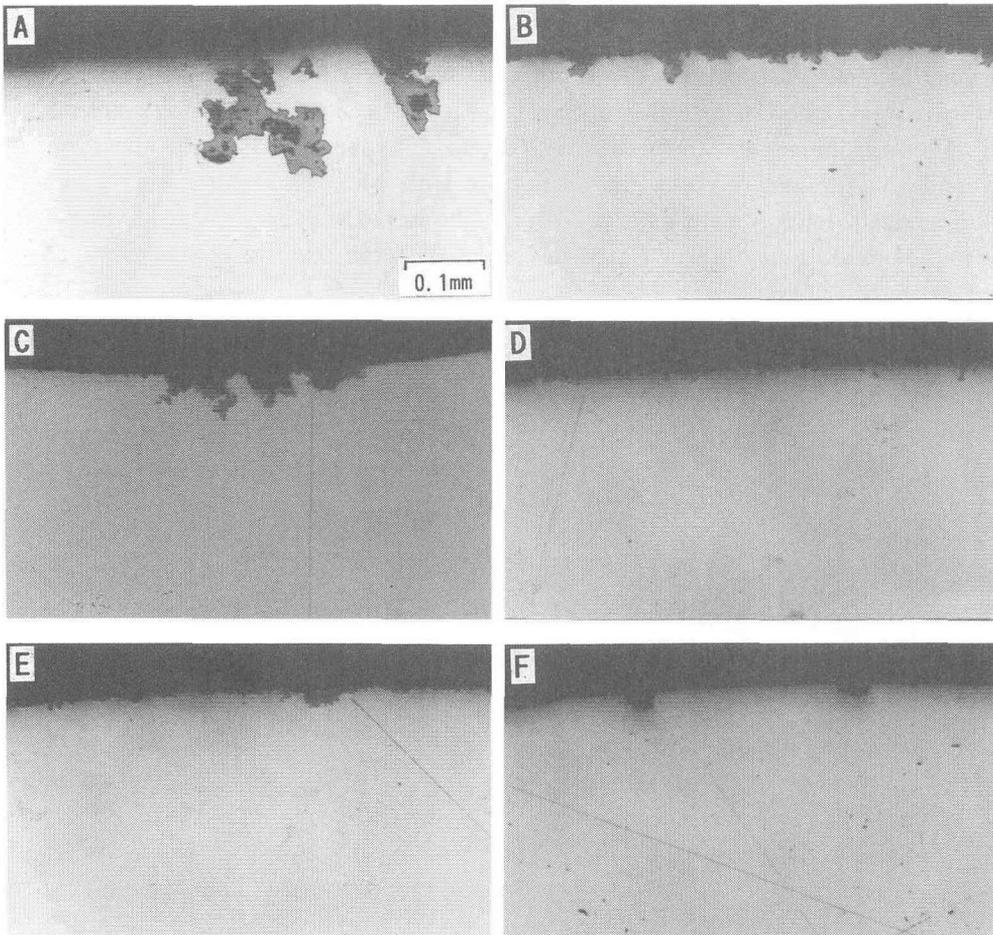
Figure 2

3. Results and Discussion

The metallic lustre of the as-received copper tubes faded with the exposure time and turned to a grey-violet color. After 20 days the top end of the copper tube formed blue corrosion products. The pretreated copper tubes maintained its metallic lustre in all areas except the top ends for 20 days. The surface of treated copper tubes turned slightly darker for BTA-, chromate- and Gliccoat T-treated copper tubes after 100 days of exposure, but no corrosion was found on the shiny untarnished area or the slightly tarnished areas of the treated copper tubes of both PD and OF copper when viewed under an optical microscope. Despite the untarnished area being greater OF copper

than PD copper, it could be concluded that the pretreatment with the organic inhibitors gave considerable protection to the copper tubes and was effective in preventing tarnishing of their surfaces. Only the top ends of the treated copper tubes were affected by the localized corrosion.

Figure 2 shows cross sections of the top ends of treated and untreated PD copper tubes. Irregular-shaped pits were observed in untreated tubes, chromic acid-treated and potassium dichromate-treated copper tubes, e. g. pictures A, B and C, respectively. These pits are nearly all plugged with cuprous oxide (the grey parts) and there are microvoids in the copper oxide (the darker parts). Numerous shallow pits were observed in both BTA-treated (D) and chromic acid plus BTA treated (E) copper tubes. No pits were detected and the surface remained smooth for the Glicoat T-treated cop-



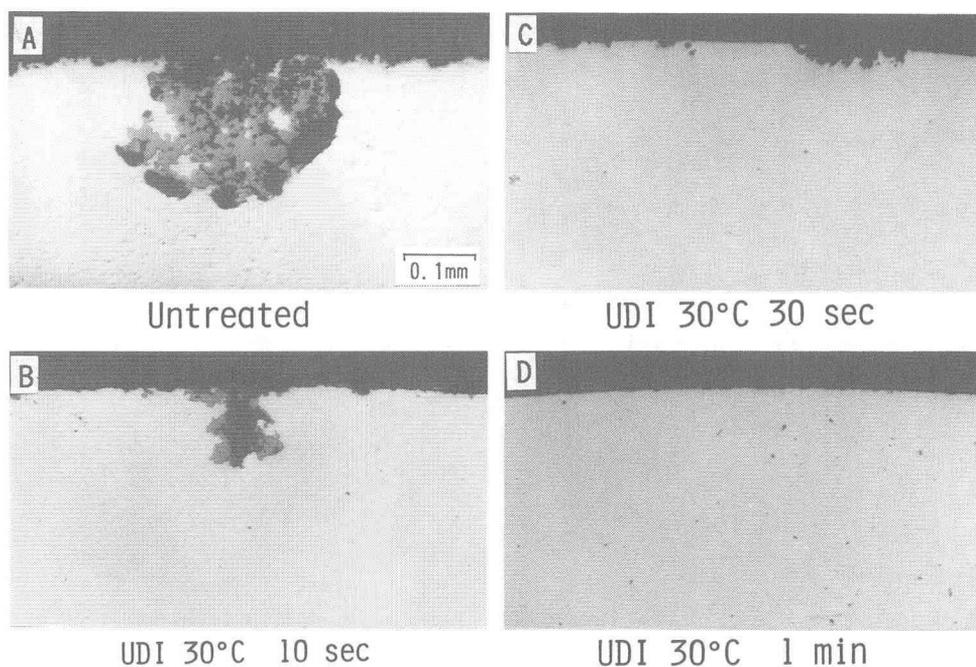
Cross-section of oxygen-free high-purity copper tubes of as-received(A, C, E) and treated with Glicoat T(B, D, F). These tubes had been exposed to humid air over 1 vol. % (A, B) formic acid, (C, D) acetic acid and (E, F) propionic acid for 20 days.

Figure 3

per tube (F).

Figure 3 shows a cross-section of the top ends of untreated and Glicoat T-treated OF copper tubes. These copper tubes were exposed to humid air over 1 vol % formic acid HCOOH (pictures A and B), acetic acid CH_3COOH (pictures C and D) and propionic acid $\text{C}_2\text{H}_5\text{COOH}$ (pictures E and F) for a period of 20 days for comparison. The corrosion rate increased in the order $\text{C}_2\text{H}_5\text{COOH} < \text{CH}_3\text{COOH} < \text{HCOOH}$. This order agrees with the dissociation constant of the acids which reflects acid strength: $-\log k$ is 3.77 for HCOOH , 4.76 for CH_3COOH and 4.87 for $\text{C}_2\text{H}_5\text{COOH}$. Because of the relative acid strengths, HCOOH causes a more rapid corrosion than the other two. With HCOOH the corrosion shows an irregular cross section, which is similar to that in the PD copper. Again, all Glicoat T-treated copper tubes show less corrosion than untreated ones. A slight penetration was seen in the Glicoat T-treated copper tube (B) in Figure 3, as compared with (F) in Figure 2, where there is no penetration. This may be due to the higher concentration of HCOOH in Figure 3.

Figure 4 shows a cross-section of untreated and Glicoat T-treated PD copper tubes with different immersion times in the Glicoat T solution. The thickness of undecylimidazole film on the copper surface varies with immersion time and it is about 0.17, 0.40 and 0.60 micron meters for 10, 30 and 60 sec, respectively. After 40 days exposure to a humid atmosphere of 0.1 vol % formic acid, the severity of the corrosion de-



Cross-section of phosphorus deoxidized copper tubes after 40 days exposure to a humid air over 0.1 vol % formic acid.

Figure 4

creased relative to the increase in thickness of the Cu-undecylimidazole film. No pittings was observed in the copper tube which was treated with Glicoat T for 60 sec.

4. Conclusions

1. This type of corrosion of both PD and OF copper tubes can be prevented by pretreatment with the organic inhibitors.
2. 2-Undecylimidazole pretreatment is more effective than benzotriazole pretreatment in inhibiting ant-nest corrosion in both PD and OF copper tubes.
3. Chromic acid and potassium dichromate pretreatment were not effective for preventing the localized corrosion.

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