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Xiaomin Wu
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Frank Gao
International Copper Association (China)

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Hydrophilic Treatments of Copper Finned Tube Evaporators

Jingchun MIN*, Xiaomin WU, Lifeng SHEN, Frank GAO

1 Department of Engineering Mechanics, Tsinghua University
Beijing 100084, China
Phone: +86-10-62784876, Email: minjc@tsinghua.edu.cn

2 Key Laboratory for Thermal Science and Power Engineering of Ministry of Education
Department of Thermal Engineering, Tsinghua University
Beijing 100084, China

3 International Copper Association (China), Ltd.
Shanghai 200020, China

ABSTRACT

Surface treatment tests were conducted on copper fins and copper finned tube evaporators for the purpose of wettability improvement. The fins used were formed using volatile fin press oil and had a smooth wavy geometry. Selected were two treatments that included the sodium hydroxide (NaOH) and potassium persulphate (K_2S_2O_8) mixed solution treatment and the air heating treatment. The surface wettability of copper fins was evaluated using the contact angle method and the durability of the surface treatments was examined through the wet/dry cycling tests. The surface wettability of copper fin evaporators was rated by splashing water on the evaporators and observing the appearance of the water. The experimental results suggest that the solution treatment can improve the surface wettability of copper fins and copper finned tube evaporators to the maximum, while the air heating treatment can improve the wettability of copper fins, but it was not so effective in promoting that of a copper fin evaporator.

1. INTRODUCTION

The evaporators currently used in room air-conditioners use aluminum fins. Bacteria and fungi inhabit the fin surface, causing contamination of the conditioned air. To improve the indoor air quality, a possible means is to replace the aluminum fins with copper fins because copper can inhibit the growth of microorganisms.

Copper has good thermal conductance but poor surface wettability. So, if an untreated copper fin evaporator is used in an air conditioner, the moisture in humid air will condense as drops on the fin surface, forming water bridges between adjacent fins, that will partly block the air flow passages in the evaporator, causing an increased air pressure drop and consequently a deteriorated cooling performance of the air conditioner. Min et al. (2000) experimentally investigated the effect of the fin surface wettability on the air pressure drop of a wavy finned tube heat exchanger under dehumidification condition; they reported that the hydrophilic treatment applied to the exchanger reduced the pressure drop by 30%. So, to use copper fins in an evaporator, it is necessary to find an effective way to make the copper fins wettable.

Various types of surface treatments have been developed to promote the surface wettability of aluminum, as described by Hong and Webb (2000). However, researches on the hydrophilic treatments of copper surface are rare. Min and Webb (2002) investigated the wetting and corrosion characteristics of hot water treated aluminum and copper fin stocks and found that the hot water soak could improve the surface wettability of both aluminum and copper surfaces. We recently performed a series of surface treatments on different kinds of copper samples that included the copper foils, copper fins and copper finned tube evaporators. The paper we published previously [Min et al. (2007)] reported the experimental results on the copper foils. It was pointed out in the paper that the improvement of copper surface wettability might be achieved through any of the following methods, namely the chemical reaction, surface adsorption, etching, and coating. To ensure the bacteriostasis of copper, the chemical
method was eventually selected. Tested included the sodium hydroxide (NaOH) and potassium persulphate (K₂S₂O₈) mixed solution treatment, air heating treatment, and others, all of which were based on the principle of generating cupric compound on copper surface. The test results supported that both the solution and the air heating treatment were effective in promoting the wetting property of copper foil.

The present article continues the previous paper and reports the test results on the copper fins and copper finned tube evaporators. Selected were two treatments that included the NaOH/K₂S₂O₈ mixed solution treatment and the air heating treatment. The purpose of this research was to establish an effective means to improve the surface wettability of a copper finned tube evaporator.

2. SOLUTION TREATMENT

This section addresses the surface treatment of copper fins and copper finned tube evaporators in a sodium hydroxide (NaOH) and potassium persulphate (K₂S₂O₈) mixed solution with formation of cupric oxide (CuO). The chemical nature of copper is inactive and no chemical reaction will occur if copper is placed in dry air or in pure water at normal temperature. The potassium persulphate is oxidant in the solution. With increase of the oxidant concentration, the film formation reaction speeds up and more crystal nucleuses form on the copper surface, as a result, the film will be thin and fine. If there is no oxidant in the solution, the film will be loose. The potassium persulphate is not stable and can be self-decomposed in alkali solution to precipitate oxygen. The decomposition rate depends on the alkali concentration and temperature. As the oxidizing temperature is raised, the oxidation process speeds up to form thin and fine films. However, a higher temperature will lead to faster decomposition of oxidants. For this reason, the solution treatment was conducted at normal temperature in this research.

2.1 Treatment of Flattened Copper Fins

The instruments and apparatuses used in the experiment included a goniometer (Shanghai Zhongchen JC2000, 0.1° resolution) and a wet/dry cycling device. The chemical reagents included the sodium hydroxide and potassium persulphate. Further, distilled water was used. The copper fins used in the experiment were smooth wavy fins formed using a volatile fin press oil. The experimental procedures were as follows:

a) Cut small pieces of copper fin and flatten them for contact angle measurement
b) Put the fin samples into a beaker with distilled water for 3-5 minutes, during this period shake the beaker from time to time to enhance the effect of decontamination
c) Take out the samples and dry them in air
d) Prepare a NaOH and K₂S₂O₈ mixed solution with a suitable concentration, immerse the samples in the solution and turn them over from time to time
e) Take out the samples after a certain period of time
f) Rinse the samples in distilled water for a minute, then air dry them
g) Measure the contact angles at three different locations on each sample, take the average as the representative contact angle
h) Subject the samples to the wet/dry cycling (30 min for one cycle, of which 5 min for wet in distilled water and 25 min for dry in air), make the contact angle measurements before cycling and after 50, 150, 300 and 500 cycles, respectively, use the measured contact angles to evaluate the durability of the wetting
i) Do the SEM examinations of the samples

Treated were 16 fin samples. The sample codes, experimental parameters, and the advancing and receding contact angles of each sample after the solution treatment are presented in Table 1. The experiment involved 4 different solution concentrations and 4 different treating times. The solution temperature was set at the room temperature (25°C), because the potassium persulfate is susceptible to dissolution at higher temperatures (Yu, 1990). The Table 1 data indicate that the higher the solution concentration and the longer the treating time, the smaller the receding contact angle. Min et al. (2000) and Min and Webb (2000, 2001) pointed out that the condensation behavior of steam on a cold wall depends mainly on the receding contact angle of the wall surface: the filmwise condensation occurs on the surface having small receding contact angle while the dropwise condensation takes place on that having great receding contact angle. We note that an untreated copper surface typically had an advancing contact angle of 80° and a receding contact angle of 40° or so. For the lowest solution concentration of NaOH 0.5g/L and K₂S₂O₈ 0.1g/L, even if the treating time reached 30 minutes, the receding contact angle of the sample was still greater than zero. With increasing the solution concentration, the receding contact angle decreased. When the
solution concentration was increased to the maximum of NaOH 5g/L and K₂S₂O₈ 1g/L, even if the treating time was 2 minutes, the receding contact angle was zero.

Table 1: Sample codes, experimental parameters and the advancing and receding contact angles of each sample after the solution treatment

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Concentration of NaOH (g/L)</th>
<th>Concentration of K₂S₂O₈ (g/L)</th>
<th>Time (min)</th>
<th>Contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C05/01-2</td>
<td>2</td>
<td></td>
<td>2</td>
<td>64</td>
</tr>
<tr>
<td>C05/01-5</td>
<td>5</td>
<td></td>
<td>5</td>
<td>65</td>
</tr>
<tr>
<td>C05/01-10</td>
<td>0.5</td>
<td>0.1</td>
<td>10</td>
<td>62</td>
</tr>
<tr>
<td>C05/01-30</td>
<td>30</td>
<td></td>
<td></td>
<td>71</td>
</tr>
<tr>
<td>C05/01-2</td>
<td>2</td>
<td></td>
<td>2</td>
<td>40</td>
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<td>C1/02-5</td>
<td>5</td>
<td></td>
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<td>63</td>
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<td>1</td>
<td>0.2</td>
<td>10</td>
<td>52</td>
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<td></td>
<td>50</td>
</tr>
<tr>
<td>C2/04-2</td>
<td>2</td>
<td></td>
<td>2</td>
<td>68</td>
</tr>
<tr>
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<td>2</td>
<td>0.4</td>
<td>5</td>
<td>65</td>
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<td></td>
<td>2</td>
<td>63</td>
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<td>C5/1-5</td>
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<td></td>
<td>5</td>
<td>63</td>
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<tr>
<td>C5/1-10</td>
<td>10</td>
<td></td>
<td>10</td>
<td>63</td>
</tr>
<tr>
<td>C5/1-30</td>
<td>30</td>
<td></td>
<td></td>
<td>67</td>
</tr>
</tbody>
</table>

The wet/dry cycling tests were conducted on four of the samples listed in Table 1. Fig. 1 illustrates the advancing and receding contact angles of each sample after some certain numbers of cycles. Note that the zero cycle means after the solution treatment but before the cycling. The receding contact angles of the C05/01-10 and C05/01-30 samples showed a decrease with the number of cycles, they were 3-5° after 50 cycles, 0° after 150 cycles, and remained zero thereafter. Whilst the receding contact angles of the C5/1-10 and C5/1-30 samples were independent of the number of cycles and maintained constant at zero throughout the cycling tests.

Fig. 2 presents the SEM photo of each sample after 500 cycles. The figure shows that on the surface of the C5/1-10 especially the C5/1-30 sample there existed a needle-like micrometer-scale structure. From the macro angle,
however, there was no significant difference among these samples. As compared to the untreated copper fin, the treated samples looked somewhat darker and uneven.

![Figure 2: SEM photo of each sample after 500 cycles](image)

### 2.2 Treatment of Un-Flattened Copper Fins

The fins used in the experiment introduced above were pressed flat (to measure the contact angles) before being treated. However, in the actual process of evaporator treatment, the evaporator fins certainly do not experience the flattening process. In order to determine the optimum parameters of the solution treatment, we conducted experiments on un-flattened copper fins. Optimum parameters shall meet two requirements, namely they should improve the hydrophilicity of copper fins to the maximum (receding contact angle is zero) and simultaneously maintain the original luster of the fins.

The experiments were conducted as below: Cut five pieces of copper fins, have four of them be treated in the solution but keep one be untreated for reference. On the basis of fully considering the results on the flattened fin samples, select the Table 2 parameters for experimenting. Set the treating time at 5 minutes, because if the time is too short, the expectant result cannot be achieved; if the time is too long, it is disadvantageous from the practical point of view. Set the solution temperature at normal temperature, because K$_2$S$_2$O$_8$ is easy to decompose at high temperature. In order to enhance the effect of cleaning, clean the copper fins in an ultrasonic tank before experimenting. The cleaning process was as follows:

a) Add an appropriate amount of water in the ultrasonic cleaning tank  
b) Set the solution temperature at 25°C and the cleaning time at 5 min  
c) Add an appropriate amount of cleaning agent (a commercial copper cleaner whose PH value is 8.5), stir it for dissolving to obtain a cleaning solution with 5% concentration  
d) After the stabilization of the cleaning solution temperature at the preset temperature, put the fin samples in the cleaning tank and start ultrasonic cleaning  
e) After the cleaning, take out the samples, wash them with clean water and then air dry them

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>NaOH Concentration (g/L)</th>
<th>K$_2$S$_2$O$_8$ Concentration (g/L)</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2.5/0.5</td>
<td>2.5</td>
<td>0.5</td>
<td>25</td>
<td>5</td>
</tr>
<tr>
<td>C5/1</td>
<td>5</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C7.5/1.5</td>
<td>7.5</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C10/2</td>
<td>10</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The surface conditions of fin samples after treatment are shown in Fig. 3. Since it was impossible to measure the contact angle, the following method was used to evaluate the wettability of fin samples, i.e., immerse the fin sample in water and then take it out, if continuous water film forms on the sample, it will be considered that the wettability has been improved to the maximum; if water drops exist on the sample, it will be considered that the wettability has not been fully improved. The results suggest that continuous films can form on the surfaces of the fin samples C7.5/1.5 and C10/2, while water drops form on the surfaces of the fin samples C2.5/0.5 and C5/1. It can be drawn from these results that (NaOH, K$_2$S$_2$O$_8$) = (7.5g/L, 1.5g/L) is the optimum concentration. As seen in Fig. 3, the fin sample C7.5/1.5 basically maintains the original luster of copper.
Based on the above results, the process flow of treatment in the NaOH/K$_2$S$_2$O$_8$ mixture was preliminarily determined as follows:

Ultrasonic cleaning (5% cleaning solution, 25°C, 5min) → washing with clean water → treatment in mixture (mixture of NaOH 7.5g/L and K$_2$S$_2$O$_8$ 1.5g/L, 25°C, 5min) → washing with clean water → dry in the air

2.3 Treatment of Copper Fin Evaporators

The evaporators used in the experiment used copper tubes and copper fins. The basic structural parameters of the evaporators were as follows: tube diameter – 9.52mm, number of tube rows – 2, tube arrangement – staggered, fin pitch - 1.55 mm, fin thickness - 0.1 mm, and fin geometry - smooth wavy. Further, the outside dimension of the evaporator body was approximately 410mm×600mm×50mm.

To get better results, evaporator samples were ultrasonically cleaned before being treated. The power of the ultrasonic cleaner was 3.0kW and the frequency was 28 kHz. The dimension of the cleaning tank was 1000mm×600mm×400mm. Inside the tank there were six (6) 2.0kW heaters (totally 12.0kW) that were used to control the temperature of the cleaning solution. The cleaning agent used was a commercial copper cleaner whose PH value was 8.5. The cleaning parameters selected were 5% cleaning solution concentration, 25°C temperature and 5 minute cleaning time.

We first treated the evaporator according to the process flow established on the basis of the experimental results with copper fins. The treatment process was completed in the cleaning tank of the ultrasonic cleaner. The procedures were as follows:

a) Add an appropriate amount of water in the ultrasonic cleaning tank
b) Set the solution temperature at 25°C and the heater in the cleaning tank will start heating the water. After the water temperature is stabilized at 25°C, take an appropriate amount of NaOH reagent, put it in the water, and stir it until it is completely dissolved. Then, take an appropriate amount of K$_2$S$_2$O$_8$ reagent, put it in the above solution, and stir it until it is completely dissolved to prepare a mixture of NaOH 7.5g/L and K$_2$S$_2$O$_8$ 1.5g/L
c) Immerse and hold the evaporator in the mixture for 5 minutes, during which shake the evaporator from time to time to accelerate the reaction
d) Take out the evaporator and wash it with clean water

We note that all water involved in the experiment was treated using a reverse-osmosis water purifier. We used the water splashing method to rate the surface wettability of the evaporator and discovered that water drops existed on the evaporator surface. This means that the optimum treatment result was not achieved. We therefore put the evaporator in the solution again, took it out after 5 minutes, cleaned it with clean water and evaluated the wettability again. The results showed that no water droplet existed on the evaporator surface, suggesting that the optimum treatment result was achieved.

The above results suggest that it is more difficult to treat an evaporator than to treat a single fin. The possible reason is that fins are densely distributed on the evaporator, which affects the cleaning and treatment results in some degrees. However, through appropriately extending the reaction time, optimum results of treatment can still be achieved.

The above evaporator had been treated twice, so another evaporator was used for treatment. The process of cleaning and treating the evaporator was the same as that for the previous evaporator, except that the treating time was set at 10 minutes. Using the water splashing method to evaluate the wettability of the treated evaporator, it was found that
the surface of the evaporator was free of water droplets, indicating that the optimum treatment result was achieved. Fig. 4 compares the behavior of water on the untreated and solution treated copper fin evaporators.

![Figure 4: Behavior of water on the untreated and solution treated evaporators](image)

Based on the above results, the process flow of evaporator treatment in the NaOH/\(\text{K}_2\text{S}_2\text{O}_8\) mixed solution can be determined as below:

- Ultrasonic cleaning (5% cleaning solution, 25°C, 5 min) → washing with clean water → treatment in mixture (mixture of NaOH 7.5g/L and K\(_2\)S\(_2\)O\(_8\) 1.5g/L, 25°C, 10 minutes) → washing with clean water → dry in the air

### 3. AIR HEATING TREATMENT

Copper can generate copper oxide (CuO) when it is heated in air. Given below is the chemical reaction:

\[
2\text{Cu} + \text{O}_2 \rightarrow 2\text{CuO}
\]

#### 3.1 Treatment of Flattened Copper Fins

The experiment included eight (8) fin samples, of which seven (7) were heated in air and one was maintained untreated for the purpose of comparison. The sample codes, experimental parameters and the advancing and receding contact angles of each sample after the air heating treatment are presented in Table 3. The experiment involved 3 different heating temperatures and 4 different heating times. It is seen from the table that the higher the heating temperature and the longer the heating time, the smaller the receding contact angles. For the 150°C heating temperature, when the heating time was 2 minutes, the receding contact angle was 11°; when the heating time was increased to 15 minutes, the receding contact angle became 0°. For the 200°C heating temperature or higher, even if the heating time was 2 minutes, the receding contact angle was 0°.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Heating temperature (°C)</th>
<th>Heating time (min)</th>
<th>Contact angle (°)</th>
<th>Advancing</th>
<th>Receding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>--</td>
<td>--</td>
<td></td>
<td>83</td>
<td>24</td>
</tr>
<tr>
<td>H150-2</td>
<td>150</td>
<td>2</td>
<td>77</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>H150-5</td>
<td></td>
<td>5</td>
<td>71</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>H150-10</td>
<td></td>
<td>10</td>
<td>88</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>H150-15</td>
<td></td>
<td>15</td>
<td>57</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>H200-2</td>
<td>200</td>
<td>2</td>
<td>41</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>H200-5</td>
<td></td>
<td>5</td>
<td>41</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>H320-2</td>
<td>320</td>
<td>2</td>
<td>38</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

The wet/dry cycling tests were carried out on four of the samples listed in Table 3. Fig. 5 shows the variations of the advancing and receding contact angles of each sample with the numbers of cycles. The receding contact angle of the H150-2 sample was 11° after the heating treatment, it decreased to 4° after 50 cycles, and further to 0° after 150 cycles.
cycles. After that, it remained unchanged at zero. The receding contact angle of the H150-5 sample was 8° after the heating treatment, it decreased to 0° after 50 cycles, and remained unchanged at zero thereafter. Whilst the receding contact angle of the sample that was heated to 320°C remained constant at zero throughout the cycling test. Besides, the receding contact angle of the untreated sample was 24° before the cycling, it decreased with increasing the number of cycles, and attained to zero after 150 cycles. After that, it remained constant at zero.

**Figure 5:** Variations of contact angles (°) with number of cycles

Fig. 6 shows the SEM photo of each sample after 500 cycles. The surface of the sample treated at 320°C was seriously oxidized and shows signs of falling off, while the surfaces of the samples heated to 150°C show no significant change before and after the cycling and looks close to that of the untreated sample.

**Figure 6:** SEM photo of each sample after 500 cycles

### 3.2 Treatment of Copper Fin Evaporator

The air heating treatment of copper fin evaporator was conducted as below: first, pre-heat the furnace to 200°C, and then put the evaporator in the furnace for treatment, during which keep the furnace temperature unchanged. After 20 minutes, take out the evaporator and air cool it. The copper fin test results showed that the 150°C treating temperature was low and could not necessarily improve the surface wettability of copper fins to the maximum degree (i.e., could not reduce the receding contact angles of copper fins to zero), while the 320°C treating temperature was too high and caused a serious oxidation of the fin surface. The 200°C treating temperature was therefore selected in the experiment. As for the treating time, considering the big thermal capacity of the evaporator and that it might take a long time for the evaporator to reach the furnace temperature, the treating time was taken to be 20 minutes for the experiment.

After the evaporator was cooled to the room temperature, the receding contact angle of the evaporator surface was roughly measured using a syringe. The result showed that the value was significantly greater than zero. In order to assure that the treated evaporator had sufficiently good wettability, further treatment was conducted on the
evaporator. The treating temperature and time selected for this secondary treatment were 240°C and 15 minutes, respectively. The result showed that the receding contact angle of the evaporator after the secondary treatment was still greater than zero.

The surface wettability of the air heated evaporator was evaluated using the water splashing method. Fig. 7 compares the appearance of water on the untreated and air heated evaporators. The figure shows that there are many water drops on the surface of the air heated evaporator, suggesting that the air heating treatment was not so effective in promoting the surface wettability of a copper fin evaporator.

![Untreated Air heated](image)

Figure 7: Appearance of water on the untreated and air heated evaporators

4. CONCLUSIONS

- Both the sodium hydroxide (NaOH) and potassium persulphate (K₂S₂O₈) mixed solution treatment and the air heating treatment are effective in promoting the surface wettability of a single copper fin, and the resulting good wettability is durable to the wet/dry cycling.
- The NaOH/K₂S₂O₈ mixed solution treatment is an effective method to improve the surface wettability of a copper fin evaporator. Under normal temperature, treating a copper fin evaporator in a mixture of NaOH 7.5g/L and K₂S₂O₈ 1.5g/L for a period of 10 minutes can improve the surface wettability of the copper fin evaporator to the maximum.
- Although the air heating treatment can improve the surface wettability of a single copper fin, it is not so effective in promoting the wettability of a copper fin evaporator. Treatment at 150°C for 20 minutes and further at 240°C for 15 minutes can still not sufficiently improve the surface wettability of a copper fin evaporator.
- It is more difficult to improve the wettability of a copper fin evaporator than to improve the wettability of single copper fin. This is true for both the solution and air heating treatments.

REFERENCES