

COPPER ARTICLE WITH PROTECTIVE COATING

This invention relates to protecting copper articles from a corrosive environment, and in particular, to protecting copper heat exchangers used in refrigerated cargo containers.

Ocean going cargo ships now carry large containers on their open decks which serve to expand the ship's utility. Many of these containers are equipped with refrigeration systems so that they can store perishable goods for relatively long periods of time. The refrigeration systems, however, are exposed to salt, air and water which causes the exposed parts to corrode at an accelerated rate. Heat exchanger surfaces used in the refrigeration systems are particularly susceptible to salt air and salt water corrosion.

In an effort to combat the harmful effects of salt, air and water, heat exchangers used in sea going containers are typically fabricated of copper. In addition, exposed surfaces of the heat exchangers have also been coated with various types of paints for added protection. These protective coatings have met with only limited success for a number of reasons. First, most coating materials do not adhere well to copper and eventually the coating will flake away to expose the copper substrate. Secondly, the coating must be relatively thin so that it does not adversely effect the heat transfer characteristics of the heat exchanger. Most thin layer coatings, however, are extremely porous and thus will not establish an impenetrable protective barrier for the underlying copper.

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As will be described in greater detail below, the present invention will be explained with specific reference to providing a protective barrier for a copper heat exchanger. However, it should be evident to one
5 skilled in the art that the invention is not limited to this specific application and can be used in connection with any copper article where the need exists to protect the article from a hostile environment or the like.

It is therefore an object of the present invention
10 to protect copper articles from a corrosive environment.

It is another object of the present invention to protect a copper heat exchanger from the harmful effects of salt air and water.

Yet a further object of the present invention is to
15 extend the life of refrigeration systems used in sea going cargo containers.

A still further object of the present invention is to provide a protective overcoating for a copper heat exchanger that will not adversely effect its heat transfer
20 properties, but yet will provide a relatively non-porous barrier to salt air and water.

Another object of the present invention is to provide a protective coating for a copper article that has improved adhesion properties.

25 Accordingly, the present invention relates broadly to a copper article, and more specifically, to a heat exchanger for use in a sea going refrigeration cargo container. The exposed surface of the articles are first treated to produce a black oxide layer over the exposed
30 surfaces. An acrylic outer layer is then electro-coated



over the oxide layer to provide a relatively thin yet non-porous barrier that exhibits extremely good adhesion and protective properties against corrosive substances.

5 For a better understanding of these and other objects of the present invention, reference is made to the detailed description of the invention which is to be read in conjunction with the following drawings, wherein:

Fig. 1 is a perspective view of one form of copper heat exchanger used in refrigerated sea going cargo
10 containers, and

Fig. 2 is a flow diagram showing the steps involved in providing a strongly adhesive, non-porous protective barrier to the exposed surfaces of the heat exchanger illustrated in Fig. 1.

15 Referring initially to Fig. 1, there is shown a fin coil heat exchanger, generally referenced 10, of the type typically used in association with refrigerated cargo containers. The heat exchanger includes one or more flow circuits 12 for carrying a refrigerant through the heat
20 exchanger unit. For the purposes of explanation, the unit illustrated in Fig. 1 contains a single flow circuit 12 consisting of an inlet line 13 and an outlet line 14 which are connected at one end of the exchanger by means of a 90° tube bend 15. It should be evident, however, that
25 more circuits may be added to the unit depending upon demands of the system. The unit further includes a series of radially disposed plate-like elements 16-16 that are spaced apart along the length of the flow circuit. The elements are supported in assembly between a pair of end
30 plates 17 and 18 to complete the assembly.

As noted above, heat exchangers of this type that are exposed to a harsh or corrosive environment are



generally fabricated of copper because of its good heat transfer properties and resistance to corrosion. Nevertheless, these copper units can and will be adversely effected when exposed to salt air and water for extended periods of time. Attempts have been made with varying degrees of success to coat these copper units with various material in an effort to extend the useful life of the unit. These coating materials oftentimes reduce the heat transfer capacity of the unit, exhibit poor adhesion properties and fail to penetrate into all areas of the unit that might be exposed to a hostile environment.

As will be explained in greater detail below, the exposed outer surfaces of the present copper heat exchanger are first pretreated to establish a black oxide coating thereon that creates a strong boundary layer much like that produced when aluminum is anodized. A thin acrylic overcoating is then electro-coated over the black oxide boundary layer to provide a strongly adhering protective barrier for extending the useful life of a unit exposed to a hostile environment. It has been found that this combination exhibits unexpected synergistic results and does not degrade the heat transfer properties of the unit. Additionally, the protective barrier is capable of penetrating deeply into remote, difficult to access areas, thus preventing early failure.

Turning now to Fig. 2, there is shown a flow process diagram depicting the process steps involved in producing a uniform protective barrier over the entire outer surface of the copper heat exchanger. Initially, the two open ends of the flow circuit are closed by suitable plugs (not shown) and the exchanger is immersed in an alkaline bath containing a strong base cleaner such as MI Clean 17 manufactured by Mitchell Bradford International, which is a division of Hubbard-Hall, Inc.

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of Waterbury, Connecticut. The bath contains a 4-7% concentration of MI Clean 17 in water and the solution is heated to a temperature of about 180°F. The heat exchanger is allowed to remain in the bath for about 5 to 10 minutes to thoroughly clean and degrease all exposed surfaces of the unit.

Upon removal from the alkaline bath, the unit is bathed in a cold water rinse 32 for about one minute or a period of time which is sufficient to remove the alkaline wash from the outer surface of the exchanger. The term cold water rinse as herein used refers to one in which the rinse water is at or about an ambient temperature.

The rinsed heat exchanger is then placed in a second acidic cleansing bath 34 for about 4 to 5 minutes to remove surface oxidations. The bath, held at an ambient temperature, contains about 10% concentration of Scone M-E Acid Brite 50 (also supplied by Hubbard-Hall, Inc.) in water. Acid Brite 50 contains about 20% by weight hydrochloric acid, 11% by weight phosphoric acid and 10% by weight sulfuric acid along with other non-acidic materials which combine to thoroughly ride the outer surfaces of the heat exchanger of unwanted oxides.

The unit, upon removal from the acid cleaning bath, is immediately placed in a cold water rinse 36 for about one minute or more to remove all trace of the acid bath from the outer surfaces of the unit.

The twice cleaned and rinsed part is now immersed in an oxidizing bath 38. The bath contains an oxidizing solution containing equal parts sodium hydroxide and sodium chloride in water. A concentration of about two pounds of oxidizer to a gallon of water is used. The oxidizer is commercially available from Hubbard-Hall, Inc.

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and is sold under the tradename Black Magic CB. The unit is allowed to remain in the bath for between 5 and 10 minutes at a bath temperature of about 180°F-210°F until all exposed surfaces of the copper are thoroughly coated
5 with a deep black colored oxide film.

The oxidation process is quickly terminated by rinsing the unit in cold water for two to three minutes and then in hot water that is heated to about 120°F for about ten or eleven minutes. The unit is given a final
10 rinse for about one to two minutes in deionized water at ambient temperature and allowed to dry. These rinses are depict at 40-42 in Fig. 2.

Upon drying, the unit is coated with an acrylic paint using commercially available coating equipment 44.
15 The paint is available from Pittsburgh Plate Glass Industries, Inc. of Springdale Pennsylvania and is sold under the tradename Powercron 810-611 or Powercron 830-611. The oxidized unit is immersed in a bath of acrylic paint and an electrical current of ~234 amps and 200 volts
20 applied to the unit. The unit is held in the bath for between nine and ten minutes to insure that all exposed and oxidized surfaces of the unit are fully covered with the acrylic overcoat to a thickness of between .0005 to .0010 inches. The unit is then removed from the bath and
25 the paint cured in an oven 48 for thirty minutes at 375°F.

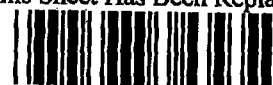
Copper parts that were oxidized and coated by the method described above were tested to determine the parts' ability to resist corrosion. The AC impedance of each coated part was first measured and recorded. The average
30 impedance of the parts was found to be about 8×10^9 ohms per square centimeter and the average thickness of the acrylic coating was about 0.0007 inches. The parts were then exposed to steam spray for a period of about 48 hours



and a second impedance measurement was then taken. The average impedance of the parts exposed to the steam was found to be about 7×10^8 ohms per square centimeter. Clearly these tests showed that the acrylic coating was
5 relatively less porous than similar coating presently in use and thus provided an improved protective barrier against corrosion. Further tests also showed that the coating exhibited improved adhesive properties and resistivity to ultraviolet radiation when compared to
10 presently employed coatings.

Although the present invention has been described with specific reference to a copper heat exchanger, it should be evident to one skilled in the art that the invention has wider applications and can be employed in
15 conjunction with any type of copper article or part that may require extended protection from a hostile environment.

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What is Claimed is:

1. A method of protecting a copper article against corrosion that includes the steps of:

5 immersing the article in an aqueous solution containing about equal parts of sodium hydroxide and sodium chloride for a period of time sufficient to establish a uniform black oxide covering exposed surfaces of the article, and

10 electrocoating said oxidized surfaces with an acrylic paint to provide a continuous protective barrier over said exposed surfaces.

2. The method of claim 1 wherein the acrylic paint is electrocoated to a uniform thickness of about between .0005 and .0010 inches.

15 3. The method of claim 1 wherein said aqueous solution contains about two pounds of sodium hydroxide and sodium chloride in each gallon of water.

20 4. The method of claim 3 wherein said article is immersed in said aqueous solution for between 4 and 6 minutes.

5. The method of claim 1 that includes the further steps of precleaning and degreasing the exposed surfaces of the article prior to the oxidization step by immersing the article in an alkaline bath and then rinsing the
25 article with water.

6. The method of claim 5 that further includes a second precleaning step of immersing the article after the first precleaning step in an acid bath to remove unwanted

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oxides from the exposed surfaces, and then washing the article with water.

7. The method of claim 6 that includes the further steps of rinsing the article after the oxidizing step in successive baths of cold water, hot water, and deionized water.

8. The method of claim 6 wherein said acid bath contains a 10% solution of sulfuric acid, phosphoric acid, and hydrochloric acid in water.

9. The method of claim 5 wherein said alkaline bath contains a 4% to 7% solution of sodium silicate in water.

10. The method of claim 1 wherein the electrocoating step lasts between nine and ten minutes so that the article has an AC impedance of between 10^8 and 10^9 ohms per cm^2 .

11. The method of claim 1 that includes the further step of curing the acrylic paint coating in an oven at 350°F to 400°F for about thirty minutes.

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