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Process for improving the corrosion resistance of copper and copper alloy radiators, and the radiators thereby obtainable.

A process for improving the corrosion resistance of copper and copper alloy radiators, characterized by the fact that the radiators, after assembly and brazing of the components, are subjected to the following operations :

- cold washing ;
- de-greasing ;
- rinsing with cold water ;
- rinsing with demineralized water ;
- filmogenous phosphatation of the surface, optionally using electrolytic means, with solution in demineralized water of phosphoric acid or derivatives thereof, chromic acid or salts thereof, an agent to reduce the hexavalent chrome to trivalent chrome and polymeric resin ;
- removal of the excess of said filmogenous phosphatation solution ;
- drying ;
- clamping of headers ;
- application of powdered paint ; and
- paint cooking.

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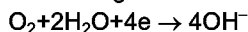
The present invention relates to a process for improving the corrosion resistance of copper and copper alloy radiators. The most significant characteristics of the process derive from the fact that the radiators are subjected to a single treatment combining the operations of phosphatation, washing, chromic passivation of the surface and formation of a film to facilitate anchoring of the paint, and from the fact of using powdered paints for subsequent painting.

As is known, the term corrosion is intended to mean that group of chemical phenomena causing the alteration of the material and degradation of its chemical and physical properties. One of the main causes of metal corrosion is the presence of impurities in the metal itself, and the fact, which is equivalent to the latter, that the metal under consideration is in contact with a different metal. Under the above conditions a short-circuiting cell is in fact created, and the less noble of the two metals, that is to say the one with the lower redox potential, passes into the solution thus corroding itself.

In the field of copper and copper alloy radiators, the danger of corrosion can be seen, for example, at the connections between copper fins and brass pipes, and at that between copper fins and leaded iron cross-members, not to mention at welding points, which are usually made using a tin-lead alloy.

In order to clarify the corrosion mechanism in copper and copper alloy radiators, let us consider the case of the iron cross-members in contact with the copper fins. Due to this contact, a cell is created, in which the two electrodes - which are short-circuiting - are Fe and Cu, and the electrolyte is the water, which contains O_2 from the air dissolved in it. The iron is a less noble metal ($E_0 = -0.450V$) than copper ($E_0 = +0.344V$), and the iron will therefore be dissolved in form of Fe^{+2} ions.

Each Fe^{+2} ion in solution corresponds to two free electrons in the iron, which migrate towards the more positive part of the metallic mass, that is to say towards the copper. The copper can then pass these electrons to one of the chemical species present in the solution, that is to say to the Fe^{+2} ions themselves, or to the oxygen; as the oxygen is an oxidant stronger than Fe^{+2} ($E_{O_2+2H_2O/4OH^-} = 0.401V$), it will undergo reduction according to the reaction



forming OH^- ions. These ions react with the Fe^{+2} ions, forming a precipitate of $Fe(OH)_2$, and subtract Fe^{+2} ions from the solution. Consequently, other Fe^{+2} ions pass into the solution, and so on. The start of precipitation of the iron hydrate $Fe(OH)_2$ marks the start of the process of corrosion of the iron, which is said to "rust".

It has been seen that the contact between two different metals favours the process of corrosion, and from this it is possible to deduct that, as in the case of radiators, should an iron structure (for instance the

panels) be covered for its protection by a thin layer of a more noble metal (copper, lead or the like), it is necessary to take great care that said protective layer be absolutely continuous. In fact, even a tiny break at one point (for example a scratch which uncovers the underlying metal) is sufficient to create a cell and start corrosion, which will then extend into the whole piece.

In order to prevent the destructive effects of corrosion on the working and integrity of this type of radiator, experience has suggested the use of certain measures aimed at limiting and preventing the phenomenon of corrosion. These measures consist substantially in causing the surface of the radiator to undergo, after assembly and welding of the component parts, washing in a buffered acid solution (using acetic, citric or chlorhydric acid), followed by spray painting with a solvent.

However, this method has not been found to be completely satisfactory, not only for technical reasons, but also for ecological and economical reasons. In the first place, in fact, the level of corrosion resistance of the radiators has shown an unsatisfactory increase. The brass pipes, for example, showed a resistance to perforation in salt spray using the test ASTM B117 not exceeding 250 hours (even the Hitachi Salt spray test gave similar results). In the second place, the use of solvents, which are generally toxic, for spray painting has raised delicate and complex problems of an ecological nature, prevention of which has had a negative effect on manufacturing costs.

For all the reasons indicated above, there is a need in this specific field for a process to improve the corrosion resistance of copper and copper alloy radiators, which does not cause damage to the environment and increased production costs.

It has now been unexpectedly found that all the above indicated aims are reached by using the process according to the present invention, which also shows additional advantages which will be more clearly seen below. In particular, the subject of the present invention is a process for improving the corrosion resistance of copper and copper alloy radiators, characterized by the fact that the radiators, after assembly and brazing of the components, are subjected to the following operations:

- cold washing;
- de-greasing;
- rinsing with cold water;
- rinsing with demineralized water;
- filmogenous phosphatation of the surface, optionally using electrolytic means, with solution in demineralized water of phosphoric acid or derivatives thereof, chromic acid or salts thereof, an agent to reduce the hexavalent chrome to trivalent chrome and polymeric resin;
- removal of the excess of said filmogenous phosphatation solution;

- drying;
- clamping of headers;
- application of powdered paint; and
- paint cooking.

Filmogenous phosphatation is performed substantially according to the BRUGAL method, described in Italian patent No. 1024649.

The radiators are preferably subjected to the process according to the present invention with their pipes set vertically with respect to the working surface.

Degreasing is preferably of an acid and alkaline type.

In the filmogenous phosphatation solution, the phosphoric acid derivatives are selected from the group comprising phosphoric anhydride, borophosphoric acid, esters of phosphoric acid, primary phosphates of Fe, Zn, Mn, Pb and combinations thereof.

In the above filmogenous phosphatation solution, the reducing agent can be of organic type and contain the hydroxylic, aldehydic, ketonic or amminic groups. This reducing agent can be selected from the group comprising: carbohydrates (polysaccharides): primary, secondary and tertiary, aliphatic, aromatic or heterocyclic alcohols; polyalcohols; aldehydes; ketones; esters; primary, secondary and tertiary, aliphatic, aromatic or heterocyclic amines; and combinations thereof.

In the filmogenous phosphatation solution, the polymeric resins can be selected from the group comprising acrylic, metacrylic and urea-formaldehyde resins. The resins can be added to the chromic phosphatation solution as a solution, emulsion or aqueous dispersion.

Removal of the excess filmogenous phosphatation solution can be performed by blowing using compressed air.

Drying can be obtained by heating in a furnace at temperatures of between 80 and 130°C for a time comprised between 1 and 30 minutes.

The powdered paint is preferably of a high reactivity epoxy type.

Application of the high reactivity epoxy paint can be performed in amounts comprised between 5 and 20 g/m² to be painted.

The granulometry of the high reactivity epoxy paint can be between 0.5 and 100 µm.

Preferably, the powder is slightly embossed.

Cooking of the paint is performed for preference at a temperature below 180°C,

The filmogenous phosphatation solution may also include accelerators, hardening agents, plastifying agents, agents inhibiting corrosion, humidifiers, anti-foam agents and sequestering agents. It may also comprise an agent to favour the reticulation and insolubility of the film selected from the group comprising tannic acid, acrylic acid, metacrylic acid, polyacrylic acids and derivatives thereof, polycarboxylic

acids, and combinations thereof.

The invention is not limited to the process for improving the corrosion resistance of radiators in copper and copper alloy. It also extends to the radiators in copper and copper alloy obtainable thereby.

The process according to the present invention has proved to be the best compromise between a number of needs, such as the corrosion resistance of radiator components (for example it should be mentioned that the pipes of radiators show a resistance to perforation in salt spray according to specification ASTM B117 of over 1000 hours), plant installation costs and unit costs of the product. The process has furthermore shown itself to be simple, reliable, with a minimum number of parameters to be controlled, easy to put into operation, and environmentally friendly.

Up to now a general description has been given of the subjects of the present invention. With the aid of the following example, a more detailed description of a specific embodiment will now be given, in order to give a clearer understanding of the objects, characteristics, advantages and possible applications of the invention.

EXAMPLE

The process according to the present invention is performed on 20 radiators of the type Fiat 160 (MONORANGO) with a size of 400 x 680 mm. The cross-members of the radiators are in copper-plated iron (thickness of the plating 20 µm). The fins are in 99.9% copper. The pipes are in brass 67. The tie rods are in AISI 304 stainless steel.

These radiators, after assembly and brazing of their components, are subjected to the following operations according to the invention:

- cold washing;
- de-greasing using an aqueous solution containing phosphoric acid;
- rinsing with cold water;
- rinsing with demineralized water;
- filmogenous phosphatation using a solution of 40% BRUGAL 5TF (marketed by the company PROCOAT, which is represented in Italy by FOSFACOL S.r.l.);
- blowing with compressed air;
- drying in a furnace for 10 minutes at 110°C;
- clamping of headers;
- application, using a compressed air spray gun, of 12 g per m² to be painted of Maicro type powdered epoxy paint (marketed by the German company Akzo), which is slightly embossed, having a granulometry of between 0.5 and 100 µm, electrostatically charged; and
- paint cooking in a furnace for 20 minutes at a temperature of 130°C.

The radiators treated using the above process

according to the present invention show a resistance to perforation under salt spray according to ASTM specification B117 of between 980 and 1000 hours.

Twenty (20) radiators with the same characteristics indicated above were protected according to the conventional method. This method provides for washing in a buffer solution of acetic acid and sodium acetate at pH 4.0-4.5, followed by washing with water, drying and spray painting (with solvent) of TEGO BEKERS alkyd paint. After the above conventional treatment, the radiators showed a resistance to perforation in salt spray according to the ASTM B117 test of between 200 and 250 hours. Their corrosion resistance is therefore greatly inferior (up to 5 times less from a chronological point of view) than that of the radiators according to the present invention.

Claims

1. A process for improving the corrosion resistance of copper and copper alloy radiators, characterized by the fact that the radiators, after assembly and brazing of the components, are subjected to the following operations:

- cold washing;
- de-greasing;
- rinsing with cold water;
- rinsing with demineralized water;
- filmogenous phosphatation of the surface, optionally using electrolytic means, with solution in demineralized water of phosphoric acid or derivatives thereof, chromic acid or salts thereof, an agent to reduce the hexavalent chrome to trivalent chrome and polymeric resin;
- removal of the excess of said filmogenous phosphatation solution;
- drying;
- clamping of headers;
- application of powdered paint; and
- paint cooking.

2. The process for improving the corrosion resistance of copper and copper alloy radiators according to claim 1, in which the radiators are subjected to the process with their pipes set vertically with respect to the working surface.

3. The process for improving the corrosion resistance of copper and copper alloy radiators according to claim 1 or 2, in which the phosphoric acid derivatives in the filmogenous phosphatation solution are selected from the group comprising phosphoric anhydride, borophosphoric acid, esters of phosphoric acid, primary phosphates of Fe, Zn, Mn, Pb and combinations thereof.

4. The process for improving the corrosion resistance of copper and copper alloy radiators according to any one of the preceding claims, in which the reducing agent in the filmogenous phosphatation solution is of an organic type and contains the hydroxylic, aldehydic, ketonic or aminic groups.

5. The process for improving the corrosion resistance of copper and copper alloy radiators according to claim 4, in which the reducing agent in the filmogenous phosphatation solution is selected from the group comprising: carbohydrates (polysaccharides); primary, secondary and tertiary, aliphatic, aromatic or heterocyclic alcohols; polyalcohols; aldehydes; ketones; esters; primary, secondary and tertiary, aliphatic, aromatic or heterocyclic amines; and combinations thereof.

6. The process for improving the corrosion resistance of copper and copper alloy radiators according to any one of the preceding claims, in which the polymeric resins in the filmogenous phosphatation solution are selected from the group comprising acrylic, metacrylic and urea-formaldehyde resins.

7. The process according to claims 1 to 6, in which the polymeric resins are added to the filmogenous phosphatation solution as a solution, emulsion or aqueous dispersion.

8. The process for improving the corrosion resistance of copper and copper alloy radiators according to any one of the preceding claims, in which removal of the excess filmogenous phosphatation solution is performed by blowing using compressed air.

9. The process for improving the corrosion resistance of copper and copper alloy radiators according to any one of the preceding claims, in which drying is obtained by heating in a furnace at temperatures of between 80 and 130°C for a time comprised between 1 and 30 minutes.

10. The process for improving the corrosion resistance of copper and copper alloy radiators according to any one of the preceding claims, in which the powdered paint to be applied is of a high reactivity epoxy type.

11. The process for improving the corrosion resistance of copper and copper alloy radiators according to claim 10, in which the granulometry of the high reactivity epoxy paint can be between 0.5 and 100 µm and the powder is slightly em-

bossed.

- 12.** The process for improving the corrosion resistance of copper and copper alloy radiators according to claim 11, in which application of the high reactivity epoxy paint can be performed in amounts comprised between 5 and 20 g/m² to be painted. 5
- 13.** The process for improving the corrosion resistance of copper and copper alloy radiators according to any one of the preceding claims, in which cooking of the powdered paint is performed at a temperature below 180°C. 10
- 14.** The process for improving the corrosion resistance of copper and copper alloy radiators according to any one of the preceding claims, in which the aqueous filmogenous phosphatation solution also includes accelerators, hardening agents, plastifying agents, agents inhibiting corrosion, humidifiers, anti-foam agents and sequestering agents. 15
- 15.** The process for improving the corrosion resistance of copper and copper alloy radiators according to any one of the preceding claims, in which the aqueous filmogenous phosphatation solution also comprises an agent to favour the reticulation and insolubility of the film selected from the group comprising tannic acid, acrylic acid, 20 metacrylic acid, polyacrylic acids and derivatives thereof, polycarboxylic acids, hydrocarboxylic acids, and combinations thereof. 25
- 16.** Radiators in copper and copper alloy, characterized by the fact that they are obtainable using the process according to claims 1 to 15. 30

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