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**DE-A-2 225 030  
FR-A-1 087 475  
FR-A-1 204 092  
FR-A-2 048 116  
US-A-3 578 508  
US-A-3 968 313**

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## Description

The present invention relates to the inhibition of corrosion in circulating water systems which include aluminium or aluminium alloy components; it is particularly advantageous when used in the operation of heating systems employing hot water radiators made of aluminium alloys.

Aluminium and its alloys have a number of attractions as materials for the construction of hot water radiators, for example their light weight and good heat emissivity characteristics. Such radiators may be manufactured in various ways, for example by casting methods, by fabrication from sheet or plate, or by assembly of suitable extruded sections. When the radiators are produced by casting, the alloy used is generally an aluminium-silicon alloy, for example Al-11% Si. For other methods, commercially pure aluminium (99.5%) can be used but its mechanical strengths and other properties are generally inadequate and alloys of aluminium are preferred. In the case of radiators fabricated from extruded sections, alloys of the aluminium-magnesium silicide group such as AA 6063 are much preferred.

It has, however, been found that aluminium and its alloys may undergo pitting corrosion when in contact with potable water drawn from domestic supplies and subjected to the temperature cycles normally encountered in radiators; in particular such pitting corrosion is liable to occur when the system includes copper-containing components so as to provide a source of copper ions in the water.

It is an object of the invention to provide a means of decreasing or avoiding the onset of such pitting attack, which seems to be dependent upon combinations of conditions of electrolyte content and aeration of the water and possibly upon other factors, which are not at present fully understood.

British Patent Specification GB—A—2013168 describes a method of inhibiting a corrosion of a body of e.g. aluminium in the presence of water by adding to the water ferrous sulphate and an organic polymer, preferably in the presence of a reducing or chelating agent, so as to deposit an even layer of ferric hydroxide on the body.

All aluminium surfaces, which are maintained in contact with hot water under conditions of aeration, develop a Bayerite-type hydrated oxide coating. It was observed that when pieces of an aluminium-11% silicon alloy from a cast radiator were subjected to water circulating in a central heating system under experimental conditions, slight pitting corrosion occurred initially; however on prolonged contact with the water, a dark coloured film developed on the surface of the metal and the pitting corrosion did not progress any further as would have been expected in the normal course of such corrosion. Indeed it became clear that the surface of the aluminium alloy had become protected against further pitting attack and that this protection was associated with the dark-coloured film.

It was at first assumed that the stifling of pitting corrosion and the dark colours of the film were caused by the incorporation into the film of silicon or a silicon compound derived from the Al—Si alloy. However, further study of the film revealed surprisingly that the dark color and the protective properties were not caused by silicon but were in fact due to the presence of very finely divided magnetite,  $\text{Fe}_3\text{O}_4$ , integral with the Bayerite layer. It has also been found that such protective film could be formed on aluminium surfaces in general and were not confined to high silicon alloys of the type involved in the initial experiment. Such films can, for example, be developed on the internal surfaces of radiators assembled from extruded sections made in alloy AA 6063 and other common extrusion alloys.

The magnetite particles were of a size less than  $0.1\text{ }\mu\text{m}$ , i.e. of colloidal dimensions and presumably originated from some colloidal solution and originated with some chance source of iron in contact with the water.

Some domestic hot water radiator systems to-day are free of iron components. In other such systems chance sources of iron, such as the water heating jacket of the boiler, exist, but may not give rise to colloidal particles of magnetite incorporated into the Bayerite film under the operating conditions.

According to the present invention, there is provided a method of reducing corrosion of the surface of an aluminium or aluminium alloy component in contact with circulating water, which method comprises providing on the surface a protective oxide layer containing finely divided particles of magnetite.

Preferably, a source of colloidal magnetite is introduced into the circulating water so as to form on the surface of the component the protective film of magnetite. Thus colloidal magnetite may be introduced into the circulating water, preferably at a concentration of from 500 ppm to 10000 ppm. Below 500 ppm, the protective film may be developed only slowly or to an insufficient extent. Amounts above 10000 ppm contaminate the circulating water without providing sufficient compensating advantages.

The method of the invention may be used to pre-treat the component before it comes in contact with the circulating water. Preferably, however, the source of colloidal magnetite is introduced into the circulating water at substantially the same time as the component, whereby there is formed on the surface thereof a protective layer of hydrated alumina containing the finely divided particles of magnetite.

The most convenient route for applying the treatment to an aluminium radiator in situ in a heating system is to dose the water in the radiator system with a magnetite-bearing material in colloidal form or in at least such a fine state of suspension that it can only remain in a settled out condition when entrapped in the growing layer of Bayerite on the surface of aluminium in contact with the water.

In one test magnetite of an average particle size of about 0.2  $\mu\text{m}$  was dispersed in water at a temperature of 70 to 75°C and circulated through an aluminium alloy pipe in the presence of a copper gauze. It was found that such magnetite was quickly absorbed into the Bayerite layer on the internal surface of the pipe. It was found that the dark-coloured Bayerite layer was highly protective and after a test under these conditions over a three month period the aluminium surface was found to be essentially free from pitting.

Preferably, a surface active agent is also introduced into the circulating water in order to assist dispersion of the colloidal magnetite in the water. We have successfully used sodium lauryl sulphate at a concentration of 0.1% by weight of the magnetite, but other agents and other concentrations might be used.

When aluminium components are present along with copper or copper alloy (e.g. brass) components in a circulating water system, galvanic corrosion of the aluminium may occur. The method of this invention is effective to reduce or prevent such galvanic corrosion, but only after a period of, perhaps, a few days when a protective layer comprising finely divided particles of magnetite has been formed. Prior to formation of this protective layer, galvanic corrosion may still occur. To prevent this, a supplementary corrosion inhibitor may be included in the circulating water. Copper passivators are well known, and can be used in conventional amounts as supplementary corrosion inhibitors. Examples are sodium mercaptobenzthiazole (smbt) and benztriazole.

It may be convenient to mix the colloidal magnetite with the surface active agent and/or the supplementary corrosion inhibitor before adding the mixture to the circulating water. The colloidal magnetite, optionally in admixture with other ingredients, may be added to the circulating water as a paste, or as capsules or tablets. Preferably the mixture is in the form of capsules coated with water-soluble gelatin.

The following Examples illustrate the invention.

#### Example 1

An aluminium coupon was directly connected to a copper coupon of equal area and immersed in Banbury tapwater at 70°C. The galvanic current generated by the Al/Cu cell was recorded, and represents a measure of the galvanic corrosion taking place.

i) when no inhibitor was present, a continuing (though fluctuating) current was recorded which did not diminish appreciably with time.

ii) in this test, various amounts of smbt were added, up to the maximum solubility of about 3 g/litre. It was found that with 0.5 g/litre or more, the current recorded rapidly fell away with time and after about 90 minutes became negligible, indicating the virtual cessation of galvanic corrosion.

iii) in this test only magnetite was added (1 g/litre) to the water, in this case it was found that the current also fell away, but more slowly than in

case ii). The current had come down to negligible values after 2 days. This result is interesting because it provides some confirmation of the observation made above that galvanic corrosion only occurs during the initial stages in a system to which magnetite has been added.

iv) finally, a test was carried out in which both magnetite and smbt were added. The current behaviour was similar to case ii) but it was found that inhibition occurred with lower amounts of smbt; in fact 0.2 g/litre was sufficient to give the same result as was achieved with 0.5 g/litre in experiment ii) and a concentration of between 0.2 and 0.5 g/litre was entirely adequate to cause rapid stifling of the galvanic activity. This result is interesting because it indicates that smbt and magnetite have some kind of "additive" effect in suppressing the galvanic corrosion.

#### Example 2

The comparative experiments of Example 1 were repeated using a test-rig system which simulates the actual use of an aluminium radiator in a circulating water system containing also copper pipes and brass fittings. The test-rig experiments confirmed the results of the beaker tests. The radiators were examined after one month's exposure in the simulated central heating system; previous experience had been that, after one month, some galvanic corrosion would have been observable in the absence of a copper passivator.

In the present case, the radiator which had been exposed to water containing 1 g/litre magnetite and 0.5 g/litre smbt showed no signs of corrosion whatsoever. Furthermore the test sample was covered with a very good black film which was determined to comprise hydrated alumina containing embedded therein the colloidal particles of magnetite.

#### Claims

1. A method of reducing corrosion of the surface of an aluminium or aluminium alloy component in contact with circulating water, which method comprises providing on the surface a protective oxide layer containing finely divided particles of magnetite.

2. A method as claimed in claim 1, wherein the component is of an aluminium-silicon alloy or an alloy of the aluminium-magnesium-silicide group.

3. A method as claimed in claim 1 or claim 2, wherein the component is a hot water radiator in a heating system.

4. A method as claimed in any one of claims 1 to 3, wherein a source of colloidal magnetite is introduced into the circulating water so as to form on the surface the protective film of magnetite.

5. A method as claimed in claim 4, wherein the source of colloidal magnetite is introduced into the circulating water at substantially the same time as the component, whereby there is formed on the surface thereof a protective layer of

hydrated alumina containing the finely divided particles of magnetite.

6. A method as claimed in any one of claims 1 to 5, wherein colloidal magnetite is introduced into the circulating water at a concentration of from 500 ppm to 10000 ppm.

7. A method as claimed in claim 6, wherein a surface active agent is also introduced into the circulating water, in order to assist dispersion of the magnetite in the water.

8. A method as claimed in any one of claims 1 to 7, wherein a supplementary corrosion inhibitor is incorporated to suppress galvanic corrosion of the component in the presence of copper or a copper alloy.

9. A method as claimed in any one of claims 6 to 8, wherein there is introduced into the circulating water at least one capsule or tablet comprising colloidal magnetite and optionally also the surface active agent and/or the supplementary inhibitor.

10. A method as claimed in claim 9, wherein the capsules are coated with water-soluble gelatin.

#### Patentansprüche

1. Verfahren zum Verhindern der Korrosion an der Oberfläche einer Aluminium- oder Aluminiumlegierungskomponente im Kontakt mit zirkulierendem Wasser, dadurch gekennzeichnet, dass man auf der Oberfläche eine Schutzoxidschicht, enthaltend feinteilige Teilchen von Magnetit, ausbildet.

2. Verfahren gemäss Anspruch 1, worin die Komponente eine Aluminium-Silicium-Legierung oder eine Legierung der Aluminium-Magnesium-Silicid-Gruppe ist.

3. Verfahren gemäss Anspruch 1 oder Anspruch 2, worin die Komponente ein Heisswasserradiator in einem Heizsystem ist.

4. Verfahren gemäss einem der Ansprüche 1 bis 3, worin eine Quelle für kolloidalen Magnetit in das Zirkulationswasser so eingeführt wird, dass es auf der Oberfläche den Schutzfilm aus Magnetit bildet.

5. Verfahren gemäss Anspruch 4, worin die Quelle des kolloidalen Magnetits in das Zirkulationswasser im wesentlichen zur gleichen Zeit wie die Komponente eingeführt wird, wodurch auf der Oberfläche der Komponente eine Schutzschicht aus hydratisiertem Aluminiumoxid, enthaltend die feinteiligen Teilchen von Magnetit, gebildet wird.

6. Verfahren gemäss einem der Ansprüche 1 bis 5, worin der kolloidale Magnetit in das Zirkulationswasser in einer Konzentration von 500 ppm bis 10.000 ppm eingeführt wird.

7. Verfahren gemäss Anspruch 6, worin ein oberflächenaktives Mittel ebenfalls in das Zirkulationswasser eingeführt wird, um die Dispergierung des Magnetits in dem Wasser zu unterstützen.

8. Verfahren gemäss einem der Ansprüche 1 bis

7, worin ein zusätzlicher Korrosionsinhibitor zur Unterdrückung einer galvanischen Korrosion der Komponente in Gegenwart von Kupfer oder einer Kupferlegierung inkorporiert wird.

9. Verfahren gemäss einem der Ansprüche 6 bis 8, worin in das Zirkulationswasser wenigstens eine Kapsel oder Tablette aus kolloidalem Magnetit und gewünschtenfalls auch dem oberflächenaktiven Mittel und/oder dem zusätzlichen Inhibitor eingeführt wird.

10. Verfahren gemäss Anspruch 9, worin die Kapsel mit wasserlöslicher Gelatine beschichtet ist.

#### Revendications

1. Procédé de réduction de corrosion de la surface d'une pièce en aluminium ou en un alliage d'aluminium en contact avec l'eau en circulation, procédé qui consiste à établir sur la surface une couche protectrice d'oxyde contenant des particules finement divisées de magnétite.

2. Procédé selon la revendication 1, dans lequel la pièce est en un alliage d'aluminium et de silicium ou un alliage du groupe aluminium-magnésium-siliciure.

3. Procédé selon la revendication 1 ou 2, dans lequel la pièce est un radiateur à eau chaude dans un système de chauffage.

4. Procédé selon l'une quelconque des revendications 1 à 3, selon lequel on introduit une source de magnétite colloïdale dans l'eau en circulation de manière à former sur la surface la pellicule protectrice de magnétite.

5. Procédé selon la revendication 4, selon lequel on introduit la source de magnétite colloïdale dans l'eau de circulation sensiblement en même temps que la pièce, de sorte que sur la surface de celle-ci est formée une couche protectrice d'alumine hydratée contenant les particules finement divisée de magnétite.

6. Procédé selon l'une quelconque des revendications 1 à 5, selon lequel on introduit la magnétite colloïdale dans l'eau en circulation en une concentration de 500 à 10.000 ppm.

7. Procédé selon la revendication 6, selon lequel on introduit également un agent tensio-actif dans l'eau de circulation afin de contribuer à la dispersion de la magnétite dans l'eau.

8. Procédé selon l'une quelconque des revendications 1 à 7, selon lequel on incorpore un inhibiteur supplémentaire de corrosion pour supprimer la corrosion galvanique de la pièce en présence de cuivre ou d'un alliage de cuivre.

9. Procédé selon l'une quelconque des revendications 6 à 8, selon lequel on introduit dans l'eau en circulation au moins une capsule ou tablette comprenant de la magnétite colloïdale et facultativement un agent tensio-actif et/ou l'inhibiteur supplémentaire.

10. Procédé selon la revendication 9, dans lequel les capsules sont enrobées de gélatine hydro-soluble.