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SUPPRESSION OF CORROSION

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The present invention is directed to a method for suppressing corrosion. More specifically, it is directed to a method wherein a surface comprising at least a major portion of metallic copper is brought into contact with a fluid comprising a material selected from the group of ammonia and ammonium hydroxide in corrosion-producing amounts and wherein the corrosion of the surface is suppressed by the addition to the fluid of an inhibiting agent.

In many operations, it is desirable to employ equipment provided with a surface or surfaces of which at least the major portion is metallic copper and to contact such surface or surfaces with fluids containing a compound selected from the group of ammonia and ammonium hydroxide. As an example of such an operation, ammonia and ammonium hydroxide per se are used commercially. As another example, fluids containing acid are conveniently neutralized by the use of ammonia or ammonium hydroxide and such fluids usually have appreciable amounts of ammonia or ammonium hydroxide present therein. In petroleum refining operations, as in the distillation of crude petroleum, acid may be liberated in the treatment of the petroleum vapors and in order to suppress the corrosion caused by the acid it is convenient to inject ammonia or ammonium hydroxide into the vapors and the fluid containing an excess of ammonia or ammonium hydroxide may then be brought into contact with metallic surfaces including a large portion of copper, such as the tubes in heat exchangers and condensers. It is more common to employ copper-containing alloys than metallic copper and such alloys are usually quite susceptible to corrosion when brought into contact with ammonia and ammonium hydroxide.

The corrosion resulting when copper and copper alloys are subjected to ammonia and ammonium hydroxide may be divided into two classes. One class may be termed surface corrosion while the other class may be designated as stress-corrosion cracking or season cracking. When copper-containing alloys are free from external and internal stress, the exposure to ammonium hydroxide or ammonia results in a surface corrosion; ammonium hydroxide produces surface corrosion at a relatively rapid rate whereas atmospheres of ammonia containing moisture attack the surfaces of copper alloys at a considerable lower rate. If the copper or copper alloy member is subjected to an internal or external stress, a stress-corrosion cracking results; stress-corrosion cracking occurs more

rapidly when the member is exposed to ammonia vapor than when exposed to ammonium hydroxide solution.

It is the principal object of the present invention to suppress the deterioration of copper and copper-containing alloys subjected to a compound of the group of ammonia and ammonium hydroxide.

In accordance with the present invention, the corrosion of copper and copper alloy members when exposed to a fluid having present therein a compound selected from the group of ammonium hydroxide and ammonia is substantially eliminated by incorporating a sulfur-containing compound in said fluid. The sulfur-containing compound is added to the fluid to inhibit its action on the copper or copper-containing alloy and in general should be in the same state as the fluid, that is to say, if the copper or copper alloy member is exposed to a liquid including a corrosion producing concentration of ammonia or ammonium hydroxide the sulfur-containing compound should also be in liquid form, while if the copper or copper alloy member is exposed to a gasiform medium including ammonia or ammonium hydroxide in a corrosion producing concentration the sulfur-containing compound should also be in a gasiform state. Many sulfur-containing compounds are known which are suitable for use in the practice of the present invention. As specific materials which are given by way of example may be mentioned hydrogen sulfide, carbon disulfide, mercaptans, such as ethyl, propyl and butyl mercaptans, sulfur dioxide and sulfur trioxide. It will be found that the concentration of sulfur-containing compound may be varied over a wide range with respect to the ammonia or ammonium hydroxide and satisfactory results obtained.

While, as stated above, the concentration of the sulfur-containing compound in the fluid comprising an NH_3 group may be varied over a wide range and satisfactory results obtained, it will usually be desirable to maintain the concentration of the sulfur-containing compound within predetermined limits. It may be pointed out that the optimum concentration of sulfur-containing compound employed in a liquid medium containing the NH_3 group and acting principally to suppress surface corrosion may be different from the concentration of sulfur-containing material in a gasiform medium which gives optimum results in suppressing stress corrosion cracking of a copper or copper-containing alloy.

The preferred ranges of concentration of

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hydrogen sulfide, butyl mercaptan and carbon disulfide to be employed in a liquid medium to suppress the surface corrosion of copper or copper-containing alloys are listed below in Table I. In this table the concentration of the sulfur-containing compound is given as mole per cent of sulfur-containing compound based on the moles of NH_3 group present in the liquid medium.

Table I

Sulfur-Containing Compound	Concentration, Mole Percent
Hydrogen Sulfide.....	.005 to 1.5
Butyl Mercaptan.....	.002 to 0.6
Carbon Disulfide.....	.01 to 1

The desirable ranges of the concentration of hydrogen sulfide, butyl mercaptan and carbon disulfide to be employed in a gasiform medium to suppress the stress-corrosion cracking of copper or copper-containing alloys are shown in the following Table II. In this table, as in the preceding table, the concentration of the sulfur-containing material is given as mole per cent of sulfur-containing material included in the gasiform medium per mole of the NH_3 group present therein.

Table II

Sulfur-Containing Compound	Concentration, Mole Percent
Hydrogen Sulfide.....	.05 to 12
Butyl Mercaptan.....	.02 to 2
Carbon Disulfide.....	.02 to 2

In order to illustrate the beneficial effects of the present invention, the following example is given:

Example

A sample of Admiralty metal (69% copper, 29% zinc, and 1% tin) was immersed in a 10 per cent by weight solution of ammonium hydroxide at room temperature for 48 hours. At the end of this period, the Admiralty metal had undergone corrosion at a rate of 0.14 inch per year. This test was repeated employing an ammonium hydroxide solution of the same concentration with 0.8 per cent of butyl mercaptan added. After 48 hours, it was found that the Admiralty metal had undergone corrosion at a rate of 0.0009 inch per year. Similar results were obtained with hydrogen sulfide and carbon disulfide. In another case, Admiralty metal under stress failed as a result of stress-corrosion cracking in an atmosphere containing ammonia after three hours of exposure. This test was repeated with 3.0 per cent by weight of butyl mercaptan added to the ammonium

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hydroxide solution over which the stressed Admiralty metal was suspended. After 194 hours of exposure, there was no evidence of failure as a result of stress-corrosion cracking. Similar results were obtained with hydrogen sulfide and carbon disulfide.

From the above example it will be seen that substantially improved results are obtained in suppressing the corrosion of a member including a major portion of metallic copper exposed to a fluid comprising ammonia or ammonium hydroxide by adding to the fluid a sulfur containing compound. The mechanism by which the sulfur-containing compound suppresses the corrosion is not understood but it is believed that upon contact of the sulfur-containing compound with the surface of the copper-containing member a chemical reaction takes place which results in a surface film which remains on the copper-containing member and protects it from further contact with the ammonia or ammonium hydroxide in the fluid. It will be understood that this postulate is presented only by way of explanation and is not intended as a limitation on the present invention.

The nature and objects of the present invention having been fully described and illustrated what I wish to claim as new and useful and to secure by Letters Patent is:

In a method wherein a non-ferrous alloy comprising a major portion of metallic copper is exposed to a fluid having present in corrosion producing amounts a compound selected from the group consisting of ammonium hydroxide and ammonia, the step of suppressing corrosion of said alloy by incorporating a mercaptan in the fluid in an amount within the range of .002 to 6 mole per cent of the compound if the fluid is a liquid and within the range of .02 to 2 mole per cent of the compound if the fluid is a gasiform medium.

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