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METHOD FOR SUPPRESSING THE CORROSION OF COPPER-CONTAINING ALLOYS IN THE PRESENCE OF AMMONIUM SALTS

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2 Claims. (Cl. 23—50)

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This invention is directed to a method for suppressing the corrosion of copper-containing alloys in the presence of ammonium salts. Specifically, it is directed to the prevention of corrosion of copper alloys in aqueous solutions containing ammonium salts.

The present application is a continuation-in-part of my copending application Serial No. 756,112, now Patent No. 2,577,626.

In many operations it is often desirable to use various types of equipment (tanks, heat exchanger and condenser tubes, valves, lines, etc.) constructed of or containing copper alloys for handling solutions containing ammonium salts. Such equipment usually suffers from severe corrosion of the copper alloys due to the chemical dissolution of the copper. The rapid destruction of the copper alloys in contact with solutions containing ammonium salts is believed to be due to the formation of highly soluble copper-ammonium complex ions.

As a result of the corrosive action of ammonium salt solutions on copper, the employers of these solutions, such as the petroleum refiner, must exercise extreme care in selection of suitable alloys for his processing equipment. Thus, where these solutions are to be used, copper alloys are usually avoided. However, as mentioned before, various services require the use of copper alloys on account of other corrosive fluids being encountered. Thus, the corrosive action of carbon dioxide in steam makes nearly mandatory the employment of copper alloys such as an alloy of copper, zinc, and tin in heat exchange equipment using corrosive steam as the heat transfer medium. Thus, when solutions of ammonium salts are employed in this type of equipment, rapid attack of the copper alloy may be suffered. Ammonium salt solutions are also widely used in solvent extraction of hydrocarbons. Here again the petroleum refiner must guard against allowing the solutions to contact copper-bearing surfaces. The aforementioned corrosion reaction generally occurs at atmospheric temperature and pressure. It is believed that higher temperatures and pressures may accelerate this reaction.

It is, therefore, the main object of the present invention to provide a process whereby the deterioration of copper alloys in the presence of aqueous solutions of ammonium salts is substantially eliminated.

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Another object of the invention is to provide a method whereby copper alloys may be employed in services where they are exposed to ammonium salt solutions.

The objects of the present invention are achieved by maintaining in corrosive ammonium salt solutions in contact with copper and its alloys a corrosion inhibiting amount of a salt of a petroleum sulfonic acid.

Briefly, the present invention involves the addition to corrosive ammonium salt solutions in contact with copper bearing metals of a quantity of a salt of an oil soluble petroleum sulfonic acid, such as an alkali metal salt of mahogany sulfonic acid, in the range between 0.001% to 5% by weight, based on the ammonium salt solution. My invention is applicable to aqueous solutions of ammonium salts of inorganic acids, such as ammonium sulfate, ammonium halide, ammonium carbonate, ammonium phosphate, etc., as well as to aqueous solutions of ammonium salts of organic acids, such as ammonium acetate, ammonium propionate, ammonium butyrate, ammonium valerate, ammonium caproate, etc.

The salts of oil soluble petroleum sulfonic acid which are suitable for use in the practice of the present invention are the alkali metal salts of mahogany sulfonic acids, such as the lithium, sodium, or potassium salts. The ammonium salts of mahogany sulfonic acids are also eminently suitable in the practice of the present invention.

The oil soluble petroleum sulfonic acids which are employed to produce the salts used in the present invention may be obtained in a manner well known to the art. The production of mahogany sulfonic acids has been disclosed widely in patent literature. It may be mentioned, however, that a conventional method for preparing these acids involves the treatment with concentrated sulfuric acid of a feed stock comprising a substantial portion of unsaturated cyclic hydrocarbons. Exemplary of the type of feed stocks which may be used are the solvent extracts resulting from solvent extraction of a distillate boiling in the lubricating oil boiling range, such as, for example, a phenol extract. The extract layer, upon treatment with strong sulfuric acid results in the formation of a layer comprising oil and

oil soluble sulfonic acids or mahogany acids, and a second layer comprising sludge particles and water soluble sulfonic acids. These two layers are then separated under the influence of gravity and the oil layer, including mahogany acids, is treated with successive portions of water to obtain the predominately oil soluble sulfonic acids. These oil soluble sulfonic acids may be freed of water and then converted into the corresponding salts by addition of a suitable hydroxide, such as sodium hydroxide or ammonium hydroxide. As a specific example, a distillate obtained from a naphthenic crude oil may be solvent extracted with a solvent having the characteristics of furfural or phenol and the extract brought in contact with sulfuric acid of approximately 98% concentration. Upon contacting the concentrated sulfuric acid with the petroleum extract, sulfonic acids are formed. The mahogany acids remain in the oil phase which separates from the acid phase.

In applying the concentrated sulfuric acid, it is customary to divide the total amount employed into a number of portions and treat the petroleum extract separately with each portion and the mahogany acids allowed to remain in the extract phase or separated, if desired, between each treat with sulfuric acid. Preferably the oil soluble sulfonic acids or mahogany acids are obtained from the acid treated extract after each portion of sulfuric acid has been added thereto.

The mechanism by which the alkaline salts of petroleum sulfonic acids are effective in preventing the corrosion of copper alloys by ammonium salt solutions is not understood, but it is believed to be due to the formation of a very thin protective film on the metal. It is understood, of course, that I do not wish to bind myself to any theory offered as an explanation of the beneficial effect.

An advantage of the process of the present invention, irrespective of the prevention of corrosion of copper and its alloys, is the ability to use existing equipment in which copper and its alloys are present in processes involving the use of ammonium salt solutions.

In order to illustrate the beneficial effects of this invention, specimens of copper-containing metal (70% copper, 29% zinc, and 1% tin) were immersed in aqueous solutions of three different ammonium salts. These tests were in progress for 24 hours at room temperature and atmospheric pressure. Air was bubbled through the solutions throughout the tests. These tests were repeated under identical conditions with small amounts of sodium sulfonates of oil soluble petroleum sulfonic acids of the type illustrated added to the aqueous solutions. The results obtained in these tests are shown in the following table:

Ammonium Salt Solution	Inhibitor Added	Corrosion Rate, Inch per Year	Per Cent Reduction
Ammonium Acetate, 5%	None	0.06297	
	0.25% Sodium Sulfonates	0.00098	98.4
	0.5% Sodium Sulfonates	0.00096	98.5
Ammonium Sulfate, 5%	None	0.06991	
	0.5% Sodium Sulfonates	0.00070	99.0
Ammonium Chloride, 5%	None	0.02056	
	0.25% Sodium Sulfonates	0.01654	19.6
	0.5% Sodium Sulfonates	0.01458	29.1

It will be observed from the data presented in the foregoing table that the addition of small amounts of sodium salts of petroleum sulfonic acids effects marked reductions in the tendencies of aqueous solutions of ammonium salts to corrode copper-containing alloys. While the reduction in the corrosivity of the ammonium acetate solution and the ammonium sulfate solution is particularly marked, the corrosivity of the ammonium chloride solution is also material.

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:

1. A method for reducing the corrosive action of a corrosive solution including water, oxygen, and ammonium salt to an article having a corrodible surface consisting predominantly of copper with minor amounts of tin and zinc in contact with said solution which comprises introducing into said solution an amount of an alkali metal salt of an oil soluble petroleum sulfonic acid sufficient to inhibit the corrosion thereof.

2. A method in accordance with claim 1 in which the amount of said alkali metal salt of an oil soluble petroleum sulfonic acid is in the range between 0.001% and 5% by weight of the corrosive solution.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,630,101	Wilkin	May 24, 1927
2,220,059	Beekhuis et al.	Nov. 5, 1940
2,238,651	Keenen	Apr. 15, 1941
2,412,633	Schwartz	Dec. 17, 1946
2,455,659	Duncan	Dec. 7, 1948