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CLEANING COMPOSITION AND A METHOD OF ITS USE

Robert G. Call, Huntington, W. Va., assignor to The Dow Chemical Company, Midland, Mich., a corporation of Delaware
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This invention pertains to a cleaning composition and a method of using the composition. More particularly it pertains to a cleaning composition and a method for removing copper deposits from steam or process equipment.

Often in process equipment a small amount of copper oxide may deposit out on the equipment. While the small amount of the oxide deposited may not create a corrosion problem, it may be necessary to remove the oxide as it may have adverse catalytic effect. Also in steam equipment oxide deposits are often obtained. Even though the steam is processed by the latest methods, it contains a small amount of oxides, such as copper and iron, which deposit out in the equipment. In heat exchangers, the deposits decrease the heat transfer coefficient. However, in steam turbines and similar close tolerance equipment it becomes much more critical. The oxides, especially copper oxide, deposit out on the buckets and the nozzles of the steam turbine decreasing the efficiency of the turbine and making it essential to periodically remove the deposits. The deposits may be removed mechanically, but the job is tedious and time consuming due to the complexity of the equipment. A solvent which will readily remove the copper oxide without having a corrosive or other deleterious effect on process equipment is therefore greatly desirable.

It is therefore an object of this invention to provide a cleaning solution for removing of copper oxide and other deposits which may be occluded by the copper oxide from process equipment and steam equipment.

Another object is to provide a process for the use of a solvent for removing these undesirable deposits.

A further object is to provide a cleaning composition concentrate which may be added to water and other solvents and used in cleaning of the equipment.

The above and other objects are attained, according to the invention, by using as a cleaning composition a mixture of an amine having the general formula:

$$NH_2\text{—}(CH_2CH_2NH)_n\text{—}H$$

where *n* is a number of 1 to 4 and a hydroxylamine mineral acid salt. By using a cleaning composition consisting essentially of from 3 to 25 weight percent of the above amine, 2 to 25 weight percent of the hydroxylamine acid salt and the remainder water, the oxide deposit of copper oxide is readily and rapidly removed from process and steam equipment without corrosive or other deleterious action to the equipment. Other deposits, such as iron oxide, which are often occluded by the copper oxide are also removed by the dissolution of the copper oxide even though these other deposits may have a limited solubility in the solvent.

The combination of the particular amine and the particular hydroxylamine mineral acid salt removes copper oxide at an unusually and unexpectedly high rate. The amine and the hydroxylamine acid salt are added to water, e.g., potable water, in amount such that a composition is obtained which contains from 3 to 25 percent of the amine and from 2 to 25 percent of hydroxylamine salt. Preferably the amounts used are such that the resulting aqueous solution obtained contains from 10 to 20 percent of the amine and from 3 to 10 percent of the hydroxylamine salt. While a composition containing as low as 5 weight percent of the amines will have approximately the same fast rate of dissolving the copper oxide as solutions containing the preferred 10 to 20 percent of the amine, the additional amine is desirable, since it has a tendency to stabilize the hydroxylamine salt at these lower limits.

While ethylenediamine and hydroxylamine sulfate are the preferred constituents of the cleaning composition, other amines having the general formula:

$$NH_2(CH_2CH_2NH)_n\text{—}H$$

where *n* is 1 to 4, such as diethylenetriamine, triethylenetetramine and tetraethylenepentamine, may be used. Also other hydroxylamine mineral acid salts such as hydroxylamine hydrochloride, hydroxylamine nitrate, and hydroxylamine acid sulfate, may be used in place of the hydroxylamine sulfate.

To clean the equipment, the equipment may be dipped in the solution if it is small enough. However, the larger pieces of equipment which do not lend themselves to this type of cleaning can be filled with the cleaning composition. For example, a heat exchanger or superheater may be pumped full of the cleaning solution and the solution maintained in the heat exchanger until the copper deposits are dissolved. A similar procedure may be used in cleaning of steam turbines or large steam equipment. The turbines can be filled with the solvent. Although agitation is not necessary, it will hasten the dissolution of the oxide. Thus, when a turbine is filled with the solution, it can be rotated by the turning gear or the solution may be circulated through the equipment by means of a pump. The same method may be applied to heat exchangers or other equipment. After the oxides have been removed, the cleaning solution is drained or pumped from the equipment and the equipment washed with water to remove any remaining solution.

Temperatures from room temperature up to 200° C. are used in the cleaning of the equipment. Generally, a temperature in the range of 65 to 80° C. is preferred. At the preferred temperature the rate with which the oxide is dissolved is rapid and substantially all of the copper deposits can be removed in a contact time of from 1 to 4 hours. At room temperatures or temperatures around 25° C. the rate at which the copper oxide is dissolved by the solution is not too great and it may require from 4 to 16 hours or even 24 hours. Above 80° C. the rate of dissolution increases rapidly and at 200° C. substantially all of the oxide may be removed in a matter of 10 to 30 minutes. However, it is generally inconvenient to heat the solution above 200° C. and also above 200° C. some decomposition of the hydroxylamine salt may be obtained under certain conditions resulting in decomposition products which may be corrosive. Since an appreciable length of time is generally required to take a large piece of equipment off stream, the advantage of being able to dissolve the deposit in a matter of 15 to 30 minutes is not very important. By the time the equipment is taken off stream and filled with the cleaning solution, the total down time will not be unduly increased by maintaining the solution in the equipment for an hour or two.

Although most process and steam equipment is made of ferruginous materials, including chromium and high alloy steels, the cleaning solutions may also be used on equipment constructed of or having parts made of nickel or cobalt or alloys of these metals, such as Inconel and Stellite. On equipment having parts of the different metals, no significant galvanic corrosion is obtained.

Generally in the preparation for the cleaning of large process equipment the amine and the hydroxylamine mineral salts are mixed together with the water prior to the introduction into the equipment. At times, however, it is more convenient to have the amine and the hydroxylamine mineral salt intermixed as a concentrate and then just add a certain amount of the mixture to water prior to adding it to the equipment. This is especially convenient when a cleaning operation is carried out at the site of equipment and the chemicals have to be transported to the site. When a concentrate is prepared and used, generally the concentration of the amine is maintained in the range of 50 to 85 weight percent with the balance being the hydroxylamine mineral acid salt. A concentrate having the above concentration will generally, when mixed with water, give the preferred ratios of the amine and the hydroxylamine in the cleaning solution.

To further illustrate the invention a high temperature steam turbine of a power company was cleaned twice applying the cleaning composition of the invention and then dismantled and inspected for adverse effects. Careful inspection of the critical areas by the power company employees and the representatives of the manufacturer of the turbine revealed no signs of corrosion or any undesirable effects found which could be attributed to the use of the solvent.

On previous occasions when the turbine has been dismantled for cleaning, it was found that the deposits on the buckets and nozzles were principally of copper oxide with a minor amount of magnetic iron oxide. After cleaning and assembling of the turbine, the turbine was operated again for a period of time until the thrust and stage pressure differential data indicated that the turbine was heavily coated with deposits. At this time the turbine was taken off stream and it was cleaned by use of a cleaning solution consisting of 18 weight percent ethylenediamine, 7½ weight percent of hydroxylamine sulfate, and the remainder water.

The solution required for the treatment of the turbine was prepared in two tanks. In each tank containing 500 gallons of water, 500 pounds of a 95 percent hydroxylamine sulfate salt and 185 gallons of 98 percent ethylenediamine were added. The constituents added to the water were heated and mixed by the injection of steam into the mixture. By the injection of steam, the tanks were heated to a temperature of 93° C. and the contents in each tank was increased to 800 gallons. The heated solution from the two tanks was pumped to the turbine which required a total of 1150 gallons to fill it. Upon filling the turbine, the pumping was continued recirculating the solution back to the tanks and then again through the equipment. The solution was circulated for approximately 5½ hours, after which it was drained from the turbine. The turbine was thoroughly flushed with water before being placed in service.

After the turbine had been cleaned, the same solution was pumped through two heat exchangers on the tube side to remove the copper oxide deposit. On the shell side a new mixture of 18 percent ethylenediamine, 7½ percent hydroxylamine sulfate and the remainder water was made and the solution recycled through the shell side of the heater for about 3 hours at a temperature of 82° C. On inspection it was found that substantially all of the deposits had been removed.

Upon operation of the turbine, the thrust and stage pressure differential data indicated that the deposits had been removed.

After approximately 3 months operation, the data indicated again that a deposit had built up in the turbine to a point where it had to be removed. The turbine was again cleaned using approximately the same procedure and the same solution as above. After the second cleaning the turbine was again operated for approximately 2½ months and then disassembled for a thorough check.

The deposits found were generally thicker on the nozzles than on the buckets and the removal of the deposits by scraping showed a copper coloration next to the metal surface. The deposits were found to consist primarily of copper oxide containing minor amounts of from approximately 2 to 4 percent of magnetic iron oxide.

Careful inspection of critical areas by both the power people and representatives of the manufacturer of the turbine revealed that use of solvent treating had no deleterious effect on the turbine.

To show the improvement in solubility of copper oxide obtained by the combination of the particular amine and hydroxylamine, a series of tests was made where one gram of cupric oxide in particulate form was placed in 100 grams of an aqueous solution in which the amounts and ratios of ethylenediamine and hydroxylamine sulfate were varied. The copper oxide in the solution was heated and maintained for 1 hour at 100° C. After the contact time, the particles of copper oxide were recovered, washed, and dried, and reweighed to determine the amount of the copper oxide which had dissolved.

The results obtained as the amount and ratios of ethylenediamine and hydroxylamine sulfate were varied as shown in the table below.

Solvent		Solubility, Percent
Ethylenediamine (Percent by wt.)	Hydroxylamine Sulfate (Percent by wt.)	
0	7.5	57
1	7.5	32
2	7.5	20
3	7.5	70
4	7.5	95
5	7.5	99.5
10	7.5	99.5
15	7.5	99.5
20	7.5	99.5
25	7.5	99.5
30	7.5	99.5
35	7.5	99.5
40	7.5	60
18	0	23
18	1	57
18	2	89
18	3	99
18	7	99.5
18	9	99.5
18	11	99.5
18	13	99.5
18	15	99.5
18	20	99.5
18	25	99.5

To illustrate the effect of temperature and contact time, a series of runs was made where 6 grams of cupric oxide was placed in 100 grams of a solution consisting of 18 percent ethylenediamine, 7.5 percent hydroxylamine sulfate, and the balance water. The solutions containing the copper oxide in particulate form were heated and maintained at temperatures of 27 degrees, 48 degrees, 65 degrees, and 80 degrees centigrade for a length of time varying from 2 to 24 hours. After the contact time, the copper oxide remaining was recovered, washed, dried and reweighed to determine the percent of the copper oxide dissolved. The results obtained are shown in the table below.

Temperature, ° C.	Length of Test (hrs.)	Weight CuO Dissolved (gms.)	Percent Compound Dissolved
27	2	2.3	38.3
27	4	2.77	46.2
27	6	2.92	48.7
27	16	4.17	69.5
27	24	4.52	75.3
48	2	4.22	70.3
48	4	5.02	83.7
48	6	5.10	85.0
48	16	5.33	88.8
48	24	5.56	92.7
65	2	4.95	82.5
65	4	5.48	91.3
65	6	5.15	85.8
65	16	5.25	87.5
65	24	5.30	88.3
80	2	5.15	85.8
80	4	5.18	86.3
80	6	4.97	82.8
80	16	5.20	86.7
80	24	5.31	88.5

Another series of runs was made where various amines and hydroxylamines were used. In the performance of these tests, 1 gram of cupric oxide was placed in 100 grams of the solution and the solution heated and maintained for one hour at 100° C. After the contact time, the remaining copper oxide was washed, dried, then weighed to determine the amount of copper oxide dissolved.

The results obtained and the pertinent data are given in the table below.

Solvent				Copper Oxide Dissolved, Wt. Percent
Amine	Wt. Percent	Hydroxylamine	Wt. Percent	
Ethylenediamine	18	Hydroxylamine sulfate.	7.5	99.5
Do	18	Hydroxylamine hydrochloride.	7.5	99.5
Do	18	Hydroxylamine acid sulfate.	7.5	99.5
Diethylenetriamine	18	Hydroxylamine sulfate.	7.5	94
Triethylenetetramine	18	do	7.5	95
Tetraethylenepentamine	18	do	7.5	91

What is claimed is:

1. A cleaning composition consisting essentially of from 2 to 25 weight percent of a hydroxylamine mineral acid salt, 3 to 35 weight percent of an amine having a general formula:

$$NH_2—(CH_2CH_2NH)_n—H$$

where n is a number of 1 to 4, and the remainder water.

2. A cleaning composition according to claim 1 wherein the amine is ethylenediamine.

3. A cleaning composition according to claim 1 wherein the amine is diethylenetriamine.

4. A composition according to claim 1 wherein the amine is triethylenetetramine.

5. A composition according to claim 1 wherein the amine is tetraethylenepentamine.

6. A copper oxide solvent consisting essentially of from 3 to 25 weight percent of ethylenediamine, from 2 to 25 weight percent of hydroxylamine sulfate, and the balance water.

7. A copper oxide solvent according to claim 6 wherein the composition consists essentially of from 10 to 20 weight percent of ethylenediamine and from 3 to 10 weight percent of hydroxylamine sulfate.

8. A copper oxide solvent consisting essentially of from 10 to 20 weight percent of ethylenediamine and from 3 to 10 weight percent of hydroxylamine hydrochloride.

9. A copper oxide solvent consisting essentially of from 10 to 20 weight percent of ethylenediamine and from 3 to 10 weight percent of hydroxylamine acid sulfate.

10. A copper oxide solvent consisting essentially of from 10 to 20 weight percent of diethylenetriamine and from 3 to 10 weight percent of hydroxylamine sulfate.

11. A copper oxide solvent composition consisting essentially of from 10 to 20 weight percent of triethylenetetramine and from 3 to 10 weight percent of hydroxylamine sulfate.

12. A copper oxide solvent composition consisting essentially of from 10 to 20 weight percent of tetraethylenepentamine and from 3 to 10 weight percent of hydroxylamine sulfate.

13. A cleaning solvent concentrate consisting essentially of from 50 to 85 weight percent of an amine having the general formula:

$$NH_2—(CH_2CH_2NH)_n—H$$

where n is a number of 1 to 4 and the remainder a hydroxylamine mineral acid salt.

14. A cleaning solvent concentrate according to claim 13 wherein the hydroxylamine mineral acid salt is hydroxylamine sulfate and the amine is ethylenediamine.

15. A process for removing copper oxide deposits from ferruginous, nickel, and cobalt base materials, which comprises contacting the equipment with a solution consisting essentially of from 2 to 25 weight percent of a hydroxylamine mineral acid salt, 3 to 35 weight percent of an amine having the general formula:

$$NH_2—(CH_2CH_2NH)_n—H$$

where n is a number of 1 to 4, and the remainder water for a sufficient length of time to dissolve the deposits.

16. A process of removing from steam equipment copper oxide deposited from the steam in the equipment, which comprises contacting the steam equipment with a solution consisting essentially of from 2 to 25 weight percent of a hydroxylamine mineral acid salt, 3 to 35 weight percent of an amine having the general formula:

$$NH_2—(CH_2CH_2NH)_n—H$$

where n is a number from 1 to 4, and the remainder water at 20° to 200° C. for a time sufficient to dissolve the copper oxide deposit.

17. A process of removing from a steam turbine copper oxide deposited from the steam, which comprises filling the steam turbine with a solution consisting essentially of from 2 to 25 weight percent of hydroxylamine mineral acid salt, 3 to 35 weight percent of an amine having the general formula:

$$NH_2—(CH_2CH_2NH)_n—H$$

where n is a number of 1 to 4, and the remainder water at a temperature of 20° to 200° C., for a time sufficient to dissolve the copper oxide deposit and subsequently removing the solvent from the turbine.

18. A process according to claim 17 wherein the amine is ethylenediamine and the hydroxylamine mineral acid salt is hydroxylamine sulfate.

19. A process according to claim 18 wherein the composition consists essentially of from 10 to 20 weight percent of ethylenediamine and from 3 to 10 weight percent of the hydroxylamine sulfate, the temperature is 65° to 80° C. and the turbine is subjected to the solution for a time of from 1 to 4 hours.

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