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3,527,609

IN-SERVICE CLEANING OF COOLING WATER SYSTEMS

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11 Claims

ABSTRACT OF THE DISCLOSURE

Circulating cooling water systems having deposits of each of iron oxide and hardness on the interior metal surfaces thereof are cleaned without being taken out of service by a two-stage method. According to this method, (1) the hardness deposits are removed by adding an alkali metal salt, or ammonium salt, of an amino polycarboxylic acid to the cooling water and adjusting the pH, if necessary, to a value in the range of 7 to about 12, and preferably 8 to about 11, circulating the resulting chelant solution until the hardness is removed; and (2) with or without displacing the chelant solution with make-up water, adding a mixture of an ammonium salt, or alkali metal salt, of an amino polycarboxylic acid and an acidifying agent to the cooling water system so as to adjust the pH to about 3 to 6, and more preferably about 4 to 5.5, circulating the acidic solution until the iron oxide is removed, and finally displacing the acidic cleaning solution with make-up water. Preferably a corrosion inhibitor is employed in the second stage of the cleaning, but may not be necessary in the first stage. Ordinarily, normal water treatment is discontinued during cleaning. It is also advisable to blow down the system before commencing cleaning operations.

BACKGROUND OF THE INVENTION

Field of the invention

The invention relates to a two-stage method of in-service cleaning of a cooling water system having each of (1) iron oxide, and (2) hardness, i.e. carbonates and/or magnesium, deposited on the interior metal surface thereof.

Description of the prior art

In the cleaning of cooling water systems it has been common practice to take the system out of service and to remove hardness and iron oxide deposits by conventional methods such as soaking with and/or circulating aqueous mineral acid solutions or an aqueous alkaline solution of an amino polycarboxylic acid such as ethylene diamine tetraacetic acid (EDTA). These methods suffer from the disadvantage that the cooling water system is generally not taken out of service until heat exchange capacity becomes very poor and this often happens just at a time that is most inconvenient for the operator, for example, during the height of a busy season.

In-service cleaning also has been attempted using an aqueous alkaline solution of an amino polyacetic acid as cleaning solution but this has not been very successful since iron oxide removal is very poor unless temperatures above about 200° F. are employed.

OBJECTS OF THE INVENTION

A principal object of the invention is to provide a method of in-service cleaning of a cooling water system having each of iron oxide and hardness deposits on the interior metal surfaces thereof.

Another object of the invention is to provide a method

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of in-service cleaning of a cooling water system that is carried out at normal cooling water temperatures. Yet a further object of the invention is to clean a cooling water system, while it is in service, by a two-stage method that is compatible with the materials of construction normally encountered, yet is highly efficient, thorough and economical.

These and other objects and advantages of the present invention will be more clearly understood by those skilled in the art becoming familiar with the following description and the appended claims.

SUMMARY OF THE INVENTION

It has now been discovered that a cooling water system having deposits of each of iron oxide and hardness on the interior metal surfaces thereof is cleaned in an eminently satisfactory manner while the system is in service upon (1) adding to the circulating system sufficient alkali metal salt or ammonium salt of an amino polycarboxylic acid to dissolve the hardness, while concurrently adjusting the pH to 7 to 12, if necessary, and preferably to pH 8 to 11, circulating the resulting chelant solution until the hardness is removed, and thereafter, (2) with or without displacing the chelant solution with make up water, adding to the cooling water system a mixture of an ammonium salt or alkali metal salt of an amino polycarboxylic acid and an acidifying agent to bring the pH to about 3 to 6, and more preferably about 4 to 5.5, circulating the acidic solution until the iron oxide is removed, and displacing the acidic cleaning solution with make up water. It is desirable to employ a corrosion inhibitor in the second stage of the cleaning. Ordinarily, normal water treatment is discontinued during cleaning. It is also advisable to blow down the system before commencing cleaning operations.

BRIEF DESCRIPTION OF THE INVENTION

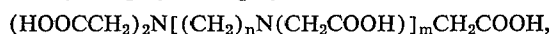
The present method is applicable to in-service cleaning of most any circulating cooling water system, for example, an open system used in connection with an air-conditioning system, where displacement of circulating aqueous liquid is economically feasible so that two-stage cleaning is possible as a practical matter, and where removal of both iron oxide and hardness is an important objective.

The acidifying agent employed in the second stage may be most any proton-donating substance which provides a substantial concentration of hydrogen ions in aqueous solution sufficient to provide the pH value desired in the range of about 3 to 6. Such proton-donating substance preferably does not form a precipitate, or not more than a slight amount of easily suspended precipitate, with dissolved salts or dissolved deposits at the concentrations found in the circulating system and is, therefore, compatible with the system.

Most any mineral acid may be used, but sulfuric acid is most preferred of these since chloride or nitrate ions may be harmful to the system. Also suitable are the organic, i.e., carboxylic acids. These include the di-, tri- or polycarboxylic acids containing from about 2 to 8 carbon atoms, including the hydroxy polycarboxylic acids all of which are appropriately described as complexing agents. Suitable polycarboxylic acids include citric acid, tartaric acid, oxalocitraconic acid, oxalic acid, malonic acid, succinic acid, malic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, diglycolic acid and phthalic acid. Of these, citric acid and tartaric acid are preferred. In general, however, it is simple and inexpensive and quite adequate to employ the lower molecular weight monocarboxylic acids such as those containing less than seven carbon atoms, e.g., formic acid, and acetic acid.

In addition, the chelant itself may be used in free acid form, obviating the need for any other acid. In this case, however, it is generally advisable to use both the acid form and the ammonium salt of the chelating agent together.

Suitable amino polycarboxylic acid chelating agents for use in the practice of the present invention include the alkylene polyamine polyacetic acids of the formula



wherein n is an integer from 1 to 4 inclusive and m is a numeral in the range of 0 to 4 inclusive and wherein up to two of the carboxymethyl groups may be replaced with a β -hydroxyethyl group and one or more of the carboxymethyl groups may be replaced by carboxyethyl groups. Specific examples of such acids which are particularly suitable are ethylenediaminetetraacetic acid (EDTA), N-hydroxyethyl ethylenediaminetriacetic acid, nitrolotri-acetic acid, N-2-hydroxyethyliminodiacetic acid, diethylenetriaminopentaacetic acid and mixtures thereof.

Any of these amino polycarboxylic acid chelating agents or a mixture thereof, are suitably employed, in the first stage cleaning, in the form of one of their alkali metal salts, normally the sodium salt, and preferably the fully neutralized salt since it imparts the greatest alkalinity. The ammonium salt may be used if desired.

Any of these same amino polycarboxylic acid chelating agents, or a mixture thereof, are suitably employed in the second stage cleaning in the form of the ammonium salt, preferably the fully neutralized salt, unless the free acid form is used to obtain the desired acidity. The alkali metal salt may also be used if desired.

The amino polycarboxylic acid chelating agents are conveniently employed in the form of an aqueous solution in which they are normally supplied commercially, typically, a 38 percent by weight aqueous solution.

A corrosion inhibitor is generally not needed during the first stage cleaning unless the cooling system contains or is suspected to contain copper or copper bearing portions in contact with the circulating liquid. In that event an inhibitor such as sodium mercaptobenzothiazol is preferably employed at a concentration of about 0.1 to about 0.5 percent by weight.

In most instances, it is preferred to employ an inhibitor to completely eliminate and reduce still further the relatively low level attack upon the metal substrate that occurs when using the present cleaning solution in the second stage. A suitable inhibitor used at a concentration of about 0.05 to 1 percent by weight is a commercial product sold by Armour and Company under the name "Armohib 31." This inhibitor is a compounded formulation that includes polyethoxylated fatty acids and similar materials, and is more thoroughly described in Chemical Abstracts, volume 62, Column 7448d (1965), the same being incorporated herein by reference.

A more preferred inhibitor which can be used in the second stage of cleaning at a concentration in the range of about 0.05 to 1 percent by weight, consists of the combination of (1) organic sulfur compound having the sulfur present in the form of $-\text{S}-$ or $\text{S}=\text{}$, e.g., N-alkylthiourea, with (2) the reaction product of dehydroabietylamine, acetophenone, paraformaldehyde and formic acid or, more generally stated, the reaction product of a nitrogen compound containing at least one active hydrogen attached to the nitrogen atom per molecule with a ketone having at least one hydrogen atom attached to the carbon atom alpha to the carbonyl group, an aldehyde, and a fatty acid, preferably prepared in the presence of an acid catalyst, at a temperature of from about 150° to about 250° F. for from 1 to about 24 hours, the same being more fully described in the copending application of William W. Bakke and Billy D. Oakes, entitled "Inhibited Metal Cleaning Composition," filed even date herewith, the disclosure thereof being incorporated herein by reference.

In carrying out the method of the invention, normal water treatment to the circulating cooling water system is discontinued during cleaning operations. It is highly advisable to blow down the system sufficiently to reduce the concentration of dissolved salts in the system to the equivalent of one to one and one-half cycles of operation in order to avoid undue consumption of chelating materials. The amino polycarboxylic acid chelating agent in the form of its sodium salt or its ammonium salt and conveniently in relatively concentrated aqueous solution, i.e., greater than about 20 percent by weight concentration, and typically, 38 percent by weight, is injected into the circulating system at any convenient point. Usually a convenient point of injection is the main feed pump. Sufficient chelating agent is injected to dissolve and complex the amount of hardness estimated to be in the system. Generally about 3.8 pounds of chelating agent, on a dry basis, is needed per pound of hardness deposits to be dissolved. Ordinarily the pH of the circulating system prior to cleaning exhibits a value of about 6.5 to 7.2, i.e., approximately neutral. Addition of the chelating agent in the form of the fully neutralized sodium salt normally brings the pH of the system to a value in the range of about 7 to about 12. If the pH is lower than 8, however, it is preferred to adjust the pH upward to the range of about pH 8-11, and more preferably to about pH 10-11, by the addition of alkaline material, preferably caustic soda.

The solution of chelating agent is allowed to circulate for at least several hours or sometimes a day or more, or until successive samples of the system taken at least 15 minutes apart and examined by chemical analysis show that there is some unspent chelating agent in the system and the degree of spentness does not change substantially during the time between samples. If the chelating agent is entirely spent or is substantially spent and the degree of spentness is still increasing, an additional quantity of chelating agent in the form of the sodium salt is preferably injected in order to complete the removal of hardness, and circulation of the cleaning solution is desirably continued until substantially complete removal of hardness has been indicated, as by additional sampling and analysis for unspent chelating agent.

When removal of hardness has been satisfactorily concluded, the cleaning solution is ordinarily displaced gradually and as rapidly as facilities permit by the addition of make-up water and concurrent blow down of a corresponding amount of circulating liquid. Sufficient displacement should be carried out to remove enough of the spent cleaning solution to bring the pH of the circulating system back to approximately the pH of the make-up water, i.e., approximate neutrality, so that acid requirements are reduced in the second stage, and also so that dissolved and chelated calcium ion does not become dissociated and precipitated when the pH is lowered below about pH 5.

In the second stage of cleaning, amino polycarboxylic acid chelating agent, preferably as the ammonium salt, though the alkali metal salt may be used, and, an acidifying agent are added to the system with or without prior mixing in a manner similar to the injection of chelating agent during the first stage. The material added by injection must bring the pH of the system down to a value in the range of about 3-6, and more preferably to a pH of about 4 to 5.5. The quantity of mixture of acidifying agent and chelating agent is an amount calculated to be sufficient to dissolve and complex or chelate the iron in the iron oxide deposits in the system. Generally about 1.9 pounds of a complexing agent such as the nitrogen-free polycarboxylic acids described, or 3.8 pounds of chelating agent, on a dry basis, are each sufficient to dissolve and tie up about one pound of iron oxide.

Again the so-prepared acidic cleaning solution is circulated for at least several hours, or sometimes a day or more, or until successive samples drawn from the sys-

tem at intervals at least 15 minutes apart indicate that dissolution of iron oxide is substantially complete. If the cleaning materials are entirely spent or if they are substantially spent and analysis indicates iron oxide is still being taken up, one or more small additions of the mixture of acidifying agent and chelating agent are made, if desired, to complete removal of iron oxide.

The cleaning operation is completed upon displacing the cleaning solution from the circulating system by addition of make-up water whereby the pH of the circulating system is brought back to a normal operating value close to pH 7.

As indicated above, if desired, a corrosion inhibitor is employed in each stage of the cleaning. Such corrosion inhibitor is conveniently dissolved in the aqueous solution chelating agent prior to injection.

In another, more simplified, embodiment of the invention, the cleaning solution is not displaced after first stage treatment to dissolve hardness but second stage cleaning is commenced simply by dropping the pH with an acidifying agent and adding additional chelating agent, preferably as the ammonium salt, or the alkali metal salt, or as the free aminopolycarboxylic acid. If the calcium concentration is substantial, as from the removal of heavy deposits of hardness, care must be taken to avoid a pH below about 5, since calcium chelate tends to dissociate and calcium may precipitate from solution under these conditions.

Because of the narrowness of the range of suitable pH values in the presence of calcium, the simplified method if of greatest advantage when systems are not so heavily coated with hardness, e.g., when they are cleaned frequently, so that lower pH values may be readily tolerated without displacing calcium chelate from the system until iron oxide removal is completed.

The following examples are illustrative and do not limit the scope of the invention.

Example 1.—An open-recirculating cooling water system containing heat exchange equipment holds 84,000 gallons of water with a recirculation rate of 24,000 gallons per minute. The make-up rate of water is 1100-1200 gallons per minute. The system contains both iron and calcium-bearing deposits primarily in the forms of Fe_2O_3 and $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$. The total estimated scale is 11,781 pounds with 7,028 pounds of $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$ and 4,753 pounds of Fe_2O_3 . Total estimated material requirements to dissolve this scale in two stages is: 66,903 pounds of 38% aqueous solution of tetra sodium EDTA, 47,530 pounds of aqueous solution of tetra ammonium EDTA (38% by weight concentration of EDTA), 8,802 pounds of anhydrous citric acid, and 84 gallons of inhibitor.

Prior to any chemical injection, the cooling tower is blown down to establish one to one and one-half cycles of concentration of dissolved mineral content. The system exhibits a pH of 6.8. At the start of the first stage of cleaning the aqueous solution of inhibited tetra sodium EDTA is steadily injected into the system through a convenient point in the circulating system just ahead of the pump. The pH is adjusted to the preferred range of 10-11 by caustic soda. The chelating material circulates throughout the system until hardness tests shows it has stopped spending, i.e., has stopped dissolving and complexing hardness.

This solution is then removed from the system by periodic displacement using the system's make-up water supply. This step is completed when the pH of the circulating water is that of the make-up water, i.e., about 7.

In the second stage of cleaning, tetra ammonium EDTA, citric acid, and inhibitor are mixed and added to the system in the same manner as the tetrasodium EDTA was added. The inhibitor consists of a mixture of (1) nonyl phenol condensed with 20 moles of ethylene oxide, (2) 1-hexyn-3-ol, (3) 1-alkyl-2-thiourea, and (4) the reaction product of dehydroabietylamine, paraformaldehyde, formic acid, and acetophenone. The material added by injection brings the pH to 5.6. This material circulates until spending has ceased, as shown by analysis, indicating that iron oxide is substantially all dissolved.

The second stage cleaning solution is then removed from the system by steady displacement using the system make-up water supply. The cleaning operation is completed when the pH of the circulating water again becomes that of the make-up water, i.e., about 6.8.

The cooling water system is successfully cleaned while in service by the foregoing recited steps as shown by the temperature of water returning from the cooling tower being below about 90° F. Further, operating experience after cleaning shows subsequent cleaning is not needed again until 5 months later.

Example 2.—The method of Example 1 is repeated on a similar cooling water system except that the amount of hardness and scale are greater than estimated, as shown by analysis for the spentness of the chelating material at each stage, indicating that chelant is entirely spent.

The remaining hardness is removed during the first stage by the injection, dissolution and circulation of an additional 8,500 pounds of 38 percent aqueous solution of tetra sodium EDTA before displacement of cleaning solution. During the second stage, there is added an additional 4,750 pounds of aqueous solution of tetra ammonium EDTA (38 percent by weight concentration of EDTA salt), 880 pounds of anhydrous citric acid, and 8.4 gallons of inhibitor, to complete the take-up of iron oxide before displacement of cleaning solution. The same excellent cleaning results are obtained as in Example 1.

Using (1) the sodium salt of any of nitrilotriacetic acid, N-hydroxy-ethyl ethylenediaminetriacetic acid, N-2-hydroxyethyliminodiacetic acid, or diethylene-triamenepentaacetic acid in place of tetrasodium EDTA; (2) the ammonium salt of such chelants in place of tetra-ammonium EDTA; and (3) oxalic acid, malonic acid, tartaric acid, formic acid, acetic acid, or sulfuric acid in place of citric acid, in Examples 1 or 2, similar eminently satisfactory cleaning results are obtained.

The method of the invention having been thus fully described, various modifications thereof will at once be apparent to those skilled in the art and the scope of the invention is to be considered limited only by the breadth of the claims hereafter appended.

I claim:

1. A two stage method of in-service cleaning of a cooling water system having each of iron oxide and hardness deposited on the interior metal surfaces thereof which comprises:

in a first stage, adding the alkali metal salt or ammonium salt of an amino polycarboxylic acid to the cooling water in an amount estimated to be sufficient to complex and dissolve substantially all the hardness deposits, whereby the pH of the system is brought to a value in the range of about 7 to 12 and a solution of the salt of amino polycarboxylic acid is formed;

circulating the solution of amino polycarboxylic acid salt until the hardness deposits are substantially all dissolved;

in a second stage, adding a mixture of the ammonium salt or alkali metal salt of amino polycarboxylic acid and an acidifying agent to the cooling water system in an amount estimated to be sufficient to complex and dissolve substantially all of the iron oxide deposits whereby the pH of the system is brought to a value in the range of about 3 to 6 and a solution of the salt of amino polycarboxylic acid is formed; circulating the resulting acidic cleaning solution of amino polycarboxylic acid salt until iron oxide is substantially all removed from the walls of the system;

and displacing the cleaning solution with make-up water whereby the pH of the cooling water system

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returns substantially to the normal operating value.

2. The method as in claim 1 in which a substantial amount of the chelant solution used in the first stage is displaced by make-up water just before commencing stage 2, whereby the pH of the cooling water being circulated returns substantially to the normal operating pH of the system.

3. The method as in claim 2 in which the cooling system is first blown down sufficiently that the concentration of dissolved hardness is substantially that obtained after from 1 to 1½ cycles of the cooling.

4. The method as in claim 2 in which the pH of the system during alkaline cleaning and immediately after addition of amino polycarboxylic acid, is adjusted to a value in the range of about 8 to 11 by the addition of caustic soda.

5. The method as in claim 2 in which the pH of the system during cleaning with the acidic mixtures is adjusted to a value in the range of about 4 to 5.5 by the addition of an acidifying agent compatible with the system.

6. The method as in claim 2 in which the acidifying agent is a proton-donating substance selected from the group consisting of sulfuric acid; and monocarboxylic acids, dicarboxylic acids, tricarboxylic acids and polycarboxylic acids having up to about 8 carbon atoms.

7. The method as in claim 2 in which normal water treatment is halted before the first stage of cleaning is commenced, and such treatment is resumed after displacement of the cleaning solution in the second stage has taken place.

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8. The method as in claim 2 in which the amino polycarboxylic acid salt employed is the sodium salt of an amino polyacetic acid.

9. The method as in claim 2 in which the amino polycarboxylic acid salt employed in stage 1 is tetrasodium ethylenediamine tetraacetic acid.

10. The method as in claim 2 in which the acidifying agent employed is a member of the group consisting of sulfuric acid, citric acid, tartaric acid, formic acid, and acetic acid.

11. The method as in claim 2 in which the pH of the cleaning solution during stage 1 is initially brought to a value in the range of about 10 to 11.

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MORRIS O. WOLK, Primary Examiner

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U.S. Cl. X.R.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,527,609 Dated September 8, 1970

Inventor(s) Joseph D. Vinso

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 44, after "and/or" insert --phosphates of calcium, and/or--.

Column 2, line 10, after "art" insert --upon--.

Column 5, line 31, delete "if" and insert --is--.

Column 7, line 11, after "cooling" insert --water--.

SIGNED AND
STAMPED

FEB 23 1971

(SEAL)

Attest:

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