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ALIPHATIC HYDROCARBON AMINE CORROSION INHIBITORS

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ABSTRACT OF THE DISCLOSURE

The present invention concerns methods and materials for inhibiting the corrosion of metal components which are contacted by corrosive substances such as the steam and steam condensate in a boiler system, in which an aliphatic amine is dispersed within the system to be treated and upon the metal surfaces to be protected. The amines employed are those having the general formula

$$CH_3-(CH_2)_n-\underset{\displaystyle RNH_2}{\underset{|}{CH}}-(CH_2)_m-NH_2$$

in which R is a divalent hydrocarbon radical containing from 1 to 4 carbon atoms, n is an integer having a value of from 1 to 18, m is an integer having a value of from 4 to 21, and the sum total of n plus m has a value from 10 to 22. A compound preferred in the practice of the invention is 9-aminomethylstearylamine.

The present invention generally relates to methods for protecting the surfaces of metal pipe and equipment which are contacted by transported, corrosive, aqueous media, or corrosive media containing aqueous components. It particularly concerns the addition of aminoalkyl substituted aliphatic amines to steam and steam condensate for the purpose of inhibiting the corrosion normally occasioned by the contact of such fluids with metal surfaces.

To simplify this discussion, references to metal and metal equipment are intended to include ferrous materials and alloys, non-ferrous alloys such as copper or nickel based alloys, and the like; and such divergent structures as pipes, tanks, valves, fittings, traps, heat exchangers, hot wells, deaerators, and the like. Similarly, while the discussion deals primarily with the corrosion caused by the contact of steam and/or steam condensate with metal surfaces, it must be realized that the inventive methods and materials are also applicable to the general treatment of metal surfaces contacted by corrosive aqueous media circulated, transported, or contained therein. However, particular benefits are realized in steam and steam condensate systems wherein it is desirable to maintain additives or foreign materials at a minimal level, and the effectiveness of the inventive materials in minute quantities is of pronounced value. In such systems, corrosion primarily results from the effects of exposure to oxygen and/or carbon dioxide entrained in the steam or condensate, and the present invention has demonstrated outstanding efficacy in combating these conditions.

Previous attempts to inhibit corrosion experienced under the described conditions have also employed aliphatic amines. In such treatments, as in the present invention, it is theorized that the treating materials are entrained in the corrosive fluids and deposit to form a protective film upon the metal surfaces. For example, U.S. Patent 2,460,259, issued to Kahler, disclosed the use of aliphatic amines of a relatively high molecular weight. While such amines yield satisfactory corrosion inhibition, they present a number of problems in respect to processing, function, economics and feeding. First, the fact that those amines which yield adequate corrosion inhibition are solids at room temperature, necessitates

their transformation to a liquid state. Secondly, effective utilization requires a composition which may be accurately metered to, and dispersed within the system to be treated. Since the extremely low water solubility of corrosion inhibiting aliphatic amines has resisted dispersion in such systems, it has been the practice to prepare dilute aqueous dispersions which are then metered and fed to the system to be treated. However, even the preparation of these dilute intermediate dispersions has entailed the utilization of these amines either in the form of salts as disclosed by U.S. Patent No. 2,712,531, issued to Maguire, or in combination with dispersant aids or emulsifiers as disclosed by U.S. Patent No. 3,088,796, issued to Kahler et al. In such cases, the salts and dispersant aids do not directly contribute to the corrosion potential of the system, and the dispersant aids may recycle to the boiler, induce foaming, or form an undesirable precipitate. Furthermore, the conversion of the amines to liquids, salts or emulsions, add appreciably to the treatment cost.

Since the majority of the foregoing problems stem from the fact that the amines providing optimum corrosion inhibition are solids at room temperature, or are difficult to disperse even when converted to a liquid form, e.g., by melting, a number of amines which are liquid at room temperature have been evaluated, e.g., low molecular weight aliphatic amines, complex branched aliphatic amines, and unsaturated aliphatic amines. However, it has been found that the low molecular weight and complex branched aliphatic amines lack satisfactory corrosion inhibition properties, while unsaturated amines undergo side reactions to yield products which are ineffective as corrosion inhibitors.

The principal objects of the present invention are the provision of:

A. Novel methods and compositions for inhibiting the corrosion of metal surfaces exposed to corrosive fluids.

B. Novel methods and compositions for inhibiting the corrosion of metal surfaces exposed to steam and steam condensate.

C. The protection of metal surfaces by means of an improved corrosion inhibition agent which is liquid at room temperature and therefore more easily metered and fed to equipment to be treated, and more readily dispersed and transported within such equipment.

D. Novel methods for treating metal surfaces with aminoalkyl substituted aliphatic amines possessing from 12 to 24 carbon atoms in the carbon chain.

E. Novel methods for treating metal surfaces with aminomethyl stearylamine.

Further objects appear in the specification and claims.

The foregoing objects are achieved by means of the addition of aminoalkyl substituted aliphatic amines to the corrosion inducing fluids which contact the metal surfaces of the equipment which is treated. It is theorized that the treating materials deposit upon the metal surfaces to provide a relatively durable protective film which may be maintained or replenished by means of the continuous or periodic addition of the treating material.

The treating materials of the present invention are liquids which may be employed and added to the treated systems without further processing, modification or intermediate handling, in concentrated or readily dilutable forms. In addition, the treating materials are readily and effectively dispersed within the treated systems and provide highly satisfactory corrosion inhibition.

The treating materials of the present invention are those aminoalkyl substituted aliphatic amines which can be represented by the following general formula:

$$CH_3-(CH_2)_n-\underset{\displaystyle RNH_2}{\underset{|}{CH}}-(CH_2)_m-NH_2$$

In which R is a divalent hydrocarbon radical having from 1 to 4 carbon atoms, n is an integer having a value from 1 to 18, m is an integer having a value from 4 to 21, and the sum total of $n+m$ has a value of 10 to 22.

Typical aminoalkyl substituted aliphatic amines are:

$CH_3(CH_2)_8CH[CH_2NH_2](CH_2)_8NH_2$
9 aminomethyl stearylamine
$CH_3(CH_2)_8CH[(CH_2)_2NH_2](CH_2)_8NH_2$
9 aminoethyl stearylamine
$CH_3(CH_2)_8CH[(CH_2)_3NH_2](CH_2)_8NH_2$
9 aminopropyl stearylamine
$CH_3(CH_2)_8CH[(CH_2)_4NH_2](CH_2)_8NH_2$
9 aminobutyl stearlyamine
$CH_3(CH_2)_7CH[CH_2NH_2](CH_2)_9NH_2$
10 aminomethyl stearylamine
$CH_3(CH_2)_{11}CH[CH_2NH_2](CH_2)_5NH_2$
6 aminomethyl stearylamine
$CH_3(CH_2)_2CH[CH_2NH_2](CH_2)_{14}NH_2$
15 aminomethyl stearylamine
$CH_3(CH_2)_4CH[CH_2NH_2](CH_2)_6NH_2$
7 amminomethyl laurylamine
$CH_3(CH_2)_6CH[CH_2NH_2](CH_2)_6NH_2$
7 aminomethyl myristylamine
$CH_3(CH_2)_7CH[CH_2NH_2](CH_2)_7NH_2$
8 aminomethyl cetylamine
$CH_3(CH_2)_9CH[(CH_2)_3NH_2](CH_2)_9NH_2$
10 aminopropyl eicosylamine
$CH_3(CH_2)_9CH[(CH_2)_4NH_2](CH_2)_{11}NH_2$
12 aminobutyl behenylamine

On the basis of the foregoing, it is evident that the treating materials of the invention are aliphatic amines possessing between 12 to 24 carbon atoms in the carbon chain, and characterized by substitution by a single aminoalkyl group. In the optimal practice of the invention, the carbon chain contains between 16 to 20 carbon atoms, and preferably 18 carbon atoms. However, this preference is based on a compromise between effective treatment with a minimum quantity of the treating material, and the cost and difficulty of preparing treating materials of higher molecular weights. It must be noted that the substituted amines of a higher molecular weight, e.g., C_{18}–C_{24}, yield greater corrosion inhibition at lower levels. However, the savings realized by virtue of the reduction in the quantity of treating material required, are consumed by the higher cost of these materials. Consequently, the C_{18} or stearyl compounds are preferred since they provide adequate corrosion inhibition at low treating levels and are moderately priced.

It has also been found that the hydrocarbon radical of the aminoalkyl substituent may contain as many as 4 carbon atoms without hindering the corrosion inhibiting power of the treating material.

It should also be noted that effective corrosion inhibition has been realized when the aminoalkyl group is substituted at a point between the 5th and 22nd carbon atom from the amino group. Similarly, the treating material may comprise a reaction product containing a plurality of isomers characterized by substitution at carbon atoms of varying distances from the amino group, e.g., an admixture of substituted amines which contains approximately equal portions of 9-aminomethyl stearylamine, and 10-aminomethyl stearylamine. Such a condition arises from the imprecise control of the synthesis reaction, and the difficulty of separating an isomer characterized by uniform substitution. It has been found that such isomeric admixtures are fully operative in the conduct of the invention. Amines in which the preponderance of substitution occurs at the central portion of the aliphatic chain are preferred, e.g., 8–11 aminomethyl stearylamines as opposed to 5-aminomethyl stearylamine or 20-aminomethyl behenylamine.

Consequently, a preferred treating composition comprises a stearylamine characterized by preponderant substitution of the 9th carbon atom from the amino group, with minor to trace quantities of isomers characterized by the substitution of the 5–8 and 10–16 carbon atoms. It must also be noted that all references to specific isomers merely indicate that those isomers preponderate in that particular composition, but that minor quantities of other isomers may be, and probably are, present, due to the difficulty of separating specific isomers from the reaction product.

The aminoalkyl substitutes amines of the present invention may be prepared in accordance with the disclosure of U.S. Patent 2,314,804, issued to Potts and Christensen. Specifically, an unsaturated fatty acid is subjected to carbonylation and oxidation reactions to yield an aldehyde which is converted to a dicarboxylic acid. The latter is then converted to the corresponding nitrile, which is in turn converted to the corresponding aminoalkyl substituted amine. For example, the synthesis of 9-aminomethyl stearylamine from oleic acid is shown below:

(1)
$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H + CO + H_2 \longrightarrow CH_3(CH_2)_8CH(CH_2)_7CO_2H \quad (CH{=}O)$$

(2)
$$+ O_2 \longrightarrow CH_3(CH_2)_8CH(CH_2)_7CO_2H \quad (CO_2H)$$

(3)
$$+ NH_3 \longrightarrow CH_3(CH_2)_8CH(CH_2)_7C{\equiv}N \quad (C{\equiv}N)$$

(4)
$$+ H_2 \longrightarrow CH_3(CH_2)_8CH(CH_2)_8NH_2 \quad (CH_2NH_2)$$

The carbonylation or formylation step above is conducted at a temperature of 50° C. in the presence of a nickel carbonyl catalyst. The air oxidation reaction (2) is conducted in the presence of a manganese salt such as the butyrate or acetate, at a temperature of 30° C. In reaction step (3) above, an excess of ammonia is bubbled through the molten fatty acid (290°). The latter reaction may be facilitated by the application of a pressure in the range of 50 p.s.i., and the use of a catalyst comprising 85% phosphoric acid. The nitrile to amine conversion is accomplished in the presence of Raney nickel at a temperature of 150° C. and a pressure of 200 p.s.i. As apparent to one skilled in art, the other aminoalkyl substituted amines contemplated for use in the invention may be prepared by the same general method.

In practicing the present invention, the quantity of the treating material which is utilized is largely dependent upon the corrosive conditions which are present in the particular systems to be treated. In systems having mildly corrosive conditions, as little as 0.01 part by weight of the treating material for each one million parts by weight of the corrosive fluids to be treated, have been found adequate to inhibit corrosion. Conversely, as much as 100 parts by weight of the treating material have been employed to inhibit corrosion in systems characterized by extremely corrosive conditions. Thus while between 0.01 to 100 parts may be employed, the treatment will normally constitute between 0.1 to 20 parts, and preferably 0.5 to 5 parts.

The actual quantity to be employed in any system of known corrosiveness is a matter readily determinable by one skilled in the art. In determining the corrosiveness of the system, and the effectiveness of a selected treatment level, the method employing steel specimens which is hereafter outlined in Example 1 may be conducted within the system to be treated. However, in determining an appropriate treatment level, the superior corrosion inhibition of specific treating materials must be considered. In this regard, it must be recalled that treating compositions of

a higher molecular weight, e.g., C_{19}–C_{24} compounds, yield higher corrosion inhibition per unit of the treating material which is employed, but are generally more costly and difficult to prepare. Consequently, in some cases it may be desirable to combine a more costly but more effective compound, e.g., an aminoalkyl behenylamine, with a less expensive compound, e.g., an aminoalkyl stearylamine, to yield a system which is characterized by both effective corrosion inhibition and modest cost. In addition, the increments of improvement in corrosion inhibition are substantially reduced, once a certain treatment level is reached. For example, 1 p.p.m. of a given treating material may reduce corrosion by 95 percent, while doubling or tripling the quantity of treatment will only yield a total corrosion reduction of 96 percent. In such cases, the cost of additional treatment must be balanced against the acceptability of limited, but greatly reduced and controlled, corrosion. However, it is advisable to feed a slight excess of the treating material to the system, in order to insure against fluctuations in the corrosion conditions which are experienced.

The treating materials of the invention are preferably continuously metered and fed to the system to be treated. In the treatment of steam or condensate in a boiler, the liquid treating materials may be fed directly to the steam header to insure distribution throughout the system. However, they may also be fed to a steam line, directly to the boiler, to the boiler feedline, or to the condensate lines or storage points. In some cases, the peculiar corrosion characteristics of the system may dictate feeding the treatment at plural points. It must be noted that when the treating material is dispersed within the steam, both the metal surfaces which are normally contacted by the steam and those surfaces normally contacted by the condensate, will be exposed to the treatment. However, when the treating material is dispersed only within the condensate, the treatment of the system forward of the point of feeding is influenced by the quantity of condensate return which is utilized as boiler makeup. Accordingly, the quantity of treating material employed must be calculated to compensate for condensate which is not returned to the boiler. When periodic or "shot" feeding of the treatment is adopted, care must be taken that the intervals between feedings, and the quantity fed, are calculated to provide adequate protection until such time as the next feeding is applied. Obviously, the method of feeding which is employed, e.g., a positive pressure pump, must be designed to overcome any pressure or flow which is present within this system, or to exploit such pressure or flow, e.g., by eduction of the treating material. Other means of feeding these materials are readily apparent to those skilled in the art.

The degree of corrosion inhibition provided by the methods and compositions of the present invention are amply demonstrated by the following examples:

EXAMPLE 1

In a simulated steam and steam condensate environment, a number of identical low carbon steel specimens or "coupons" were exposed to the environment for a period of two days, both with and without the inventive treatment. In the absence of treatment the average penetration of the specimens was 21.5 mils, while the penetration was reduced by 92%, to 1.75 mils, when 1 p.p.m. of 9-aminomethyl stearylamine was maintained in the system.

In the foregoing and subsequent accelerated corrosion tests, a flow of conednsate (0.035 feet per second) having a temperature of 150° F. and a pH of 4.7, was maintained past the steel specimens. The condensate contained 150 p.p.m. of carbon dioxide and less than 0.1 p.p.m. of dissolved oxygen.

EXAMPLE 2

Example 1 was repeated with the quantity of 9-aminomethyl stearylamine increased to 2 p.p.m. The average penetration of the specimens was 0.75 mil per year and demonstrates a 97.5% reduction in corrosion.

In the following examples, the prescribed quantities of treating compositions were fed to the steam header of a boiler. The treating materials were pumped from a 50 gallon stroage tank and dispersed directly within the steam header. The pump employed was a piston pump producing a pressure adequate to prevail against the internal pressure of the header, i.e., 500 p.s.i. in the present case.

EXAMPLE 3

Two p.p.m. of 9-aminomethyl stearylamine combined with minor quantities of aminomethyl stearylamine isomers substituted at the 6th to 8th, and the 10th to 15th carbon atoms, were maintained in the system.

EXAMPLE 4

Ten p.p.m. of 6-aminomethyl laurylamine were maintained in the system.

EXAMPLE 5

Four p.p.m. of the 7-aminomethyl myristylamine were maintained in the system.

EXAMPLE 6

Three p.p.m of 8-aminomethyl cetylamine were mainmaintained in the system.

EXAMPLE 7

0.5 p.p.m. of 12-aminobutyl behenylamine were maintained in the system.

EXAMPLE 8

One p.p.m. 9-aminomethyl stearylamine and 0.5 p.p.m of 12-aminobutyl behenylamine were maintained in the system.

The treatments of Examples 3–8 all yielded highly satisfactory corrosion inhibition at the prescribed levels.

It is apparent that novel methods for the substantial reduction or inhibition of the corrosion of metal surfaces exposed to corrosive fluids are provided by the present invention. It is further apparent that various modifications, alterations and substitutions may be made in the present invention without departing from the spirit of the invention as defined by the following claims.

I claim:

1. In a system containing metal components contacted by a corrosive fluid, a method of inhibiting the corrosion of said components, comprising dispersing in said fluid an aliphatic amine having the formula:

$$CH_3-(CH_2)_n-\underset{\displaystyle RNH_2}{\underset{|}{CH}}-(CH_2)_m-NH_2$$

in which R is a divalent hydrocarbon radical containing from 1 to 4 carbon atoms, n is an integer having a value from 1 to 18, m is an integer having a value from 4 to 21, and the sum total of n plus m has a value from 10 to 22, in an amount adequate to reduce said corrosion, and contacting the surfaces of said components with said fluid and said aliphatic amine.

2. A method of inhibiting the corrosion of metal components contacted by steam and steam condensate, comprising dispersing in said steam and said steam condensate, an aliphatic amine having the formula:

$$CH_3-(CH_2)_n-\underset{\displaystyle RNH_2}{\underset{|}{CH}}-(CH_2)_m-NH_2$$

in which R is a divalent hydrocarbon radical containing from 1 to 4 carbon atoms, n is an integer having a value from 1 to 18, m is an integer having a value from 4 to 21, and the sum total of n plus m has a value from 10 to 22,

in an amount adequate to reduce said corrosion, and contacting the surfaces of said components with said steam and steam condensate and said aliphatic amine.

3. A method as claimed in claim 2 in which said aliphatic amine consists primarily of 9-aminomethyl stearylamine.

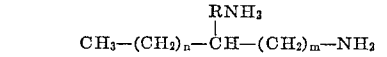
4. A method as claimed in claim 2 in which said aliphatic amine is an admixture of the isomers of aminomethyl stearylamine.

5. A method as claimed in claim 2 in which said aliphatic amine is dispersed in said steam.

6. A method as claimed in claim 2 in which said aliphatic amine is dispersed in said steam condensate.

7. A method as claimed in claim 2 in which said amount is equal to between 0.01 to 100 parts by weight for each 1,000,000 parts of said steam and said steam condensate.

8. A corrosion inhibiting composition consisting essentially of an aqueous dispersion of an aliphatic amine having the formula:



in which R is a divalent hydrocarbon radical containing from 1 to 4 carbon atoms, n is an integer having a value from 1 to 18, m is an integer having a value from 4 to 21, and the sum total of n plus m has a value from 10 to 22.

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