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3,029,125

INHIBITION OF CORROSION IN RETURN STEAM CONDENSATE LINES

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7 Claims. (Cl. 21—2.7)

This invention relates to a new and improved method for inhibiting corrosion in steam and condensate return systems.

It is well known that steam lines and steam condensate lines are subject to corrosion which is very difficult to control. This corrosion is apparently due, to a large extent, to carbon dioxide and oxygen in the boiler-steam-condensate system. Carryover from the boiler water can also increase the corrosion. The problem of corrosion of the internal surfaces of steam condensate return lines has been recognized for many years. Generally, the difficulties that have been experienced are the pitting, grooving and ultimate deterioration of sections of the condensate return system and the plugging of constrictions in the system with the insoluble products of corrosion. To properly evaluate the actual cost of return line corrosion, it is necessary not only to consider the loss in terms of labor, curtailed production and the cost of the material destroyed, but also to weigh effects in terms of inefficient operation of fouled equipment.

Experimental studies by various investigators indicate that dissolved carbon dioxide and oxygen are responsible for practically all the corrosion in the condensate lines. The various expedients that have been devised for combatting this attack are as follows:

(1) The use of corrosion resistant alloys, which is generally prohibitive from a cost standpoint.

(2) Minimizing the amount of carbon dioxide and oxygen in the condensate either by venting or pretreatment of the boiler feedwater.

(3) Chemical treatment of the condensate.

It is known to use a readily volatile alkaline amine material for protection against corrosion in steam and return condensate lines but the results obtained with such amines have sometimes left much to be desired, particularly in steam and condensate systems of great length or in tall buildings.

Moreover, these amines to be effective, are usually required in amounts which are roughly proportional to the carbon dioxide content of the condensate. Where the return of condensate to the boiler constitutes a minor fraction of the boiler feed, such treatment often becomes economically impractical.

Where high pressure steam is required to operate industrial devices, such as turbines, it has been the experience of the art that certain treatments will undergo decomposition and form deposits on the surfaces of the devices which, in many instances, will necessitate costly shutdowns and repairs.

It would be desirable to have a chemical treatment capable of being applied to any part of a steam or condensate return system at small, economical dosages and have beneficial results obtained in all cases.

One of the objects of the present invention is to provide a new and improved method of inhibiting corrosion in return steam condensate lines.

Another object of the invention is to provide compositions for the treatment of steam condensates which produce improved results in preventing or minimizing corrosion in steam lines, traps, condensers, valves and in other parts of steam systems such as turbine blades.

A further object is to provide corrosion inhibiting compositions which are stable under conditions of atmospheric and superatmospheric steam generation and will

not form deposits on the surfaces of valves, turbine blades and similar equipment.

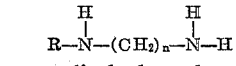
A very useful object of the invention is to furnish a chemical treatment which may be applied at any place in steam and condensate return systems and still provide adequate corrosion protection to such systems. Other objects will appear hereinafter.

It has been found that the corrosion in steam and condensate return systems may be prevented or substantially mitigated by treating such systems with a corrosion inhibiting amount of a water dispersible reaction product of a low molecular weight alkylene oxide and a substituted alkylene diamine. These materials are effective when added either to the boiler feedwater, to the steam lines, or to the condensate return lines. When added to the boiler feedwater it is generally necessary to add a slightly excessive amount to insure that enough of the chemical steam distills into the steam and condensate return systems. Generally, however, it is preferred to add the treatment to the steam condensate line since it is this part of the system where corrosive attack is the severest and the smallest amounts of the treatment are the most effective. From a practical standpoint, the chemical is most conveniently applied to the boiler feedwater.

The amount of treatment should be at least 1 part per million of the corrosion inhibiting chemical by weight of the steam or steam condensate, preferably 2 to 5 parts per million and even more preferably 10 to 25 parts per million. The dosage will, of course, vary depending on the conditions of the system and other variable factors and hence, dosages as high as 50 to 100 parts per million may be necessary under extraordinary corrosive conditions.

The employment of the corrosion inhibiting chemicals in accordance with this invention is applicable to the generation of steam at various temperatures and pressures. Good results can be obtained where steam is generated under atmospheric conditions, subatmospheric conditions or superatmospheric conditions. In most cases, steam is generated at pressures from atmospheric up to 1500 pounds per square inch or more and the corresponding temperatures.

The substituted alkylene diamines which are used as starting materials in preparing the compositions useful in the practice of the invention have the following general formula



wherein R is an acyclic hydrocarbon radical containing from 10 to 32 carbon atoms and n is an integer from 2 to 6.

The radical R is conveniently derived from a saturated or unsaturated fatty group. Such groups as dodecyl, tetradecyl, hexadecyl, octadecyl, octadecenyl, and octadecadienyl may be substituents with good results being obtained in each instance. Extremely good results are afforded when R is a mixture of alkyl radicals such as are found in vegetable oils and animal fats. Coco, soya and tallow are examples of such mixed natural radicals.

The diamine portion of the compounds described above may be one of any number of the known diamines. Ethylene diamine, 1,2-propylene diamine, 1,3-propylene diamine and hexamethylene diamine are several examples.

The substituted alkylene diamines may be prepared by several different techniques. For instance, the alkylene diamines may be alkylated with an alkyl halide to produce the desired product. Such a method is illustrated in Kyrides U.S. Patent 2,246,524. Another method is to react an alkylamine with acrylonitrile and then hydrogenate whereby an alkyl substituted propylene diamine is produced. Commercially available N-alkyl propylene di-

amines are the products manufactured by the Armour Chemical Division under the trade name, "Duomeens." Specific Duomeens are N-lauryl propylene diamine; N-coco propylene diamine; N-soya propylene diamine and N-tallow propylene diamine.

The substituted alkylene diamines thus described are capable of being reacted with varying amounts of several of the well known low molecular weight alkylene oxides, such as ethylene oxide, 1,2-propylene oxide, butylene oxide or the like, to produce products varying in their physical and chemical properties. To be suitable for present purposes, the oxyalkylated, substituted alkylene diamines must be water dispersible to the extent that 5% by weight or more forms a uniform dispersion in aqueous media. This is usually accomplished by oxyalkylating 1 mol of diamine with 1 to 4 mols of ethylene oxide or other alkylene oxide to produce the degree of water dispersibility desired.

The oxyalkylation of the products may be performed by any one of several well known methods. Since there are three reactive hydrogen atoms in the alkyl substituted diamines the oxyalkylation could conceivably take place at any of the sites. Hence, one mol of an alkylene oxide could react with any one of the three hydrogen atoms to produce a mixture of oxyalkylated products.

The alkyl substituted propylene diamines when reacted with 1 to 4 mols and preferably 2 to 3 mols of ethylene oxide have proven to be outstanding corrosion inhibitors for steam and condensate return systems. Several of these reaction products are listed below in Table I.

TABLE I

Composition No.	Alkyl Substituted Propylene Diamine	Mols of Ethylene Oxide	Water Dispersible	
			Yes	No
I	N-tallow propylene diamine	3	X	
II	do	2	X	
III	do	1	X	
IV	N-soya propylene diamine	3	X	
V	N-coco propylene diamine	3	X	
VI	N-lauric propylene diamine	4	X	
VII	N-coco propylene diamine	2	X	

In addition to the water dispersible products of low molecular weight alkylene oxides and substituted alkylene diamines certain aliphatic carboxylic acid salts of these compositions may also be employed as corrosion inhibitors for steam and condensate return systems. The salt forming aliphatic carboxylic acids should not exceed 10 carbon atoms in chain length. For purpose of classification the acids may be divided into four classes:

I. Aliphatic monocarboxylic acids
II. Aliphatic dicarboxylic acids
III. Hydroxy substituted carboxylic acids
IV. Hydroxy substituted polycarboxylic acids

In class I such acids as acetic, propionic, n-butyric, isobutyric, n-heptylic, caprylic and pelargonic acids may be used. Examples of class II are oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic and sebacic acids. Glycolic, gluconic, glyceric and lactic acids are illustrative of class III. Class IV would include such acids as malic and citric.

The salts, in some instances, have the property of making the reaction products more dispersible where dispersibility is an important consideration, and in some instances tend to render the products water soluble. This latter feature is desirable when boiler feedwater applications are contemplated. The salts will become dissociated from the oxyalkylated substituted amine reaction product during the process of being steam distilled under conditions of use. In certain cases improved corrosion inhibiting compositions are afforded by the salts of the reaction products.

For purposes of illustration, several aliphatic carboxylic acid salts of the alkyl substituted propylene diamines listed in Table I are shown below in Table II.

TABLE II

Composition No.	Composition No. Table I	Aliphatic Carboxylic Acid	Mol Ratio Reaction Product: Acid
VIII	I	acetic acid	1:1
IX	I	lactic acid	1:1
X	I	citric acid	1:1
XI	III	butyric acid	1:1
XII	IV	malic acid	1:1
XIII	V	succinic acid	1:1
XIV	I	malonic acid	2:1
XV	I	adipic acid	1:1

The salts listed in Table II were prepared by heating the compositions in Table I, which ranged from viscous liquids to pastes, and adding the acid, with continued heat, until a homogeneous product was produced.

When the compositions are to be used commercially it is often desirable to prepare a formulated product using water as diluent. In order to insure such water dilutions against freezing and to provide a uniformly stable product it is usually preferable to use a low molecular weight aliphatic alcohol as a co-solvent.

A typical formula was prepared having the following composition.

Composition XVI

Components:	Percent by weight
Composition I, Table I	20
Isopropanol	20
Water	60

The formula was prepared by dissolving Composition I, Table I into the isopropanol and then adding the water. This produced a formulation that was cloudy but homogeneous and was stable on standing at 10° F., 70° F. and 120° F. for 24 hours. It could be readily dispersed in water, at concentrations up to 50% by weight with only moderate stirring. Such dispersions remained homogeneous after standing for several days at room temperature. While it is good practice to dissolve the oxyalkylated substituted diamine reaction product into the alcohol before adding the water, the formulation may be prepared by using any mixing order with good formulas being produced.

When boiler feedwater applications are contemplated it is sometimes helpful to formulate the compositions of the invention with boiler antifoams. The compositions of the invention will not produce foaming or priming when used at the concentrations recommended herein, but in the event high concentrations occur in the boiler water, the use of antifoams is a safeguard to insure good operation of the boiler. Antifoams that may be used are those described in U.S. Patents 2,575,298; 2,626,243; 2,575,276; 2,609,344 and 2,717,881. Only a few parts per million of these antifoams in the boiler water are required to insure against any harmful foaming.

Evaluation of the Invention

(A) *Screening tests.*—The material to be tested was added, at a concentration of 100 parts per million, to 350 ml. of deionized water contained in a 400 ml. beaker. The beaker was held in an oil bath at a temperature of about 145° F. The solution was stirred at about 1750 r.p.m. with centrifugal-type glass stirrers. A mixture of CO_2 and air was bubbled through the solution during the test. A mild steel specimen was sandblasted, weighed, and placed in the solution overnight. The weight loss of the specimen was then determined. A similar test,

called the blank, was made under identical conditions except that no corrosion inhibitor was added to the water. The data from these screening tests are presented in Table III as percent protection compared with the blank test.

TABLE III

Composition:	Percent protection
Composition I, Table I	93
Composition IX, Table II	93
Sebacic acid	11
Sodium hexametaphosphate	19
Octadecyl urea	0

From the above it is evident the compositions of the invention provided superior corrosion protection as against the poor or slight protection afforded by other inhibitors tested.

(B) *Experimental condensate corrosion tests.*—This series of corrosion tests were made in an apparatus designed to simulate a severely corrosive condition which might be encountered in a steam condensate system. In this apparatus a synthetic condensate was produced in a glass tower by aerating heated distilled water with a mixture of carbon dioxide and air This condensate and a solution of the treating chemical were proportioned into a test container by gravity feed. A number of steel test coupons were suspended in the latter and the liquid was mildly agitated with a paddle stirrer. At periodic intervals a test specimen was removed from the bath and the weight loss determined. The temperature, free carbon dioxide and dissolved oxygen of the synthetic condensate, and the treatment concentration were controlled throughout the test.

The corrosion test specimens consisted of 1 inch x 2 inch panels which were sheared from a single sheet of 22 gauge cold rolled mild steel. All specimens were uniformly sandblasted before being immersed in the bath.

Agitation of the liquid was initiated and the water in the bath was heated to and thermostatically controlled at 150°±1° F. The free carbon dioxide and dissolved oxygen of the water were maintained at 45±4 parts per million and 3.5±0.2 parts per million, respectively.

A complete, detailed description of the test apparatus and method is described in the article, "A Laboratory Method for the Study of Steam Condensate Corrosion Inhibitors," by H. I. Patzelt, Corrosion, January 1953.

The following examples illustrate the results obtained in the evaluation of test specimens using treating chemicals within the scope of the invention.

EXAMPLE I

The test was first run without any inhibitor. Specimens were removed daily for 6 days and the successive corrosion losses found to be 121, 210, 327, 463, 570 and 691 milligrams respectively. In a parallel test Composition I, Table I was added to the system at 25 parts per million. The successive daily weight losses for the first 5 day period were 2.4, 3.5, 3.3, 4.7 and 4.2 milligrams.

EXAMPLE II

In this series the two compositions, Composition VIII, Table II and Composition IX, Table II were each tested separately at 10 parts per million. At the end of the 6th day the weight losses were 221 and 121 milligrams, respectively.

The corrosive conditions maintained in these tests when compared with most industrial condensate return systems are extremely severe. Inhibitors giving only good to fair results in the test in most cases give outstanding results in actual use at lower dosages.

(C) *Foaming tests.*—Foaming tests on several corrosion inhibitors were conducted in experimental boilers. Zeolite softened Chicago tap water was treated with $NaHCO_3$, NaCl, Na_2SO_4 and Na_2HPO_4 to give the following analysis:

	G.p.g.
Hardness (as $CaCO_3$)	0.0
Methyl orange alkalinity (as $CaCO_3$)	15.0
Cl	5.0
SO_4	30.0
PO_4	0.18
D.S.	50.0

The inhibitor was added to the water, and the solution was evaporated in the boiler at pressure until carryover occurred. The results of these tests are presented in Table V. The figures for dissolved solids at carryover indicate the relative foaming properties; the higher the figure the lower the foaming tendency.

Neither of the materials tested promoted foaming.

TABLE V

Foaming Tests on Corrosion Inhibitors

Inhibitor	Concentration, p.p.m.	D.S. at Carryover g.p.g.
None		182
Composition I, Table I	5	266

(D) *Effect on brass.*—The screening test method (A above) was used. Brass specimens in place of the steel were suspended in deionized water. Rather than running a percent comparison against the blank, weight losses in milligrams were determined. Composition XVI showed a weight loss of only 13.2 milligrams.

EXAMPLE III

This test was conducted in an actual boiler system to determine whether Composition XVI would be detrimental to normal boiler operation. The test boiler generated a total of 800,000 to 1,000,000 pounds of steam per day at 125 pounds per inch. Composition XVI was fed by dispersing 1 gallon into 30 to 40 gallons of condensate return and injecting it directly into the steam header. The dosage for the entire test period was maintained at 10 parts per million of the steam.

A by-pass corrosion test loop was installed in front of one of the condensate return pumps. This loop was approximately 3,000 feet from the boiler and 400 to 700 gallons passed through per day. The specimen was a 1 inch pipe nipple which was placed in the system with appropriate fittings.

The test was run for one month at the end of which time inspection revealed corrosion rates of the specimen were being satisfactorily controlled. A sample of condensate was collected from the by-pass loop and analysis showed it to contain 2.0±0.6 parts per million of Composition XVI. Of interest is the fact that the sample thus taken was at a point most remote from the boiler. There was no evidence of deposits forming in the system and no unusual foaming occurred in the boiler.

The expression "water dispersible" as used herein means a material which in water or other aqueous media does not form a true solution yet it is capable of remaining in a suspended condition at the concentrations herein specified for relatively long periods of time. These suspensions may or may not be colloidal.

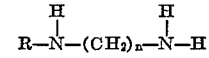
It should be noted that optimum results in evaluating compositions provided in accordance with the invention have been obtained with fully oxyalkylated long chain hydrocarbon polyamines in which all of the active hydrogen atoms attached to nitrogen atoms have been substituted by hydroxy lower alkyl groups.

The invention is hereby claimed as follows:

1. A process of inhibiting corrosion in steam and condensate return systems in which the steam and condensate are carried by ferrous metal pipes normally sus-

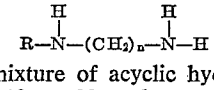
ceptible to corrosion which comprises introducing into such systems a corrosion inhibiting amount of a compound from the group consisting of hydroxyalkylated alkylene diamines containing a single long aliphatic hydrocarbon chain having from 10 to 32 carbon atoms attached to one of the nitrogen atoms and hydroxyalkylated with from 1 to 4 mols of a lower alkylene oxide for each mol of said diamine to link hydroxyalkylene groups to at least one of the nitrogen atoms to the extent that at least 5% by weight of said hydroxyalkylated diamine is water dispersible, and the salts of said hydroxyalkylated diamines with aliphatic carboxylic acids containing not more than 10 carbon atoms from the group consisting of aliphatic monocarboxylic acids, aliphatic dicarboxylic acids, hydroxy aliphatic monocarboxylic acids and hydroxy aliphatic polycarboxylic acids, said carboxylic acids containing only carbon, hydrogen and oxygen atoms, said compounds being further characterized by the fact that the initial alkylene diamines prior to hydroxyalkylation contain 2 to 6 carbon atoms connecting the amino nitrogen atoms.

2. A process of inhibiting corrosion in steam and condensate return systems in which the steam and condensate are carried by ferrous metal pipes normally susceptible to corrosion which comprises introducing into such systems a corrosion inhibiting amount of an hydroxyalkylation reaction product of from 2 to 3 mols of a lower alkylene oxide per mol of an alkylene diamine of the formula



wherein R is an acyclic hydrocarbon radical containing from 10 to 32 carbon atoms and n is an integer from 2 to 6, said alkylene diamine being hydroxyalkylated with said lower alkylene oxide to the extent that at least 5% by weight of the resultant hydroxyalkylated diamine is water dispersible.

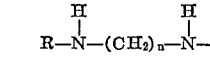
3. A process of inhibiting corrosion in steam and condensate return systems in which the steam and condensate are carried by ferrous metal pipes normally susceptible to corrosion which comprises introducing into such systems a corrosion inhibiting amount of an hydroxyethylation reaction product of from 2 to 3 mols of ethylene oxide per mol of an alkylene diamine of the formula



wherein R is a mixture of acyclic hydrocarbon radicals containing from 10 to 32 carbon atoms normally occurring in vegetable oils and fats and n is an integer from 2 to 3, said alkylene diamine being hydroxyethylated to the extent that at least 5% by weight of the resultant hydroxyethylated diamine is water dispersible.

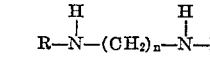
4. A process of inhibiting corrosion in steam and condensate return systems in which the steam and condensate are carried by ferrous metal pipes normally susceptible to corrosion which comprises introducing into such systems a corrosion inhibiting amount of at least 1 part per million of the reaction product of ethylene oxide and N-tallow propylene diamine in a mol ratio of about 3:1.

5. A process of inhibiting corrosion in steam and condensate return systems in which the steam and condensate are carried by ferrous metal pipes normally susceptible to corrosion which comprises introducing into such systems a corrosion inhibiting amount of an aliphatic carboxylic acid salt of an hydroxyalkylation reaction product of from 1 to 4 mols of a lower alkylene oxide per mol of an alkylene diamine of the formula



wherein R is an acyclic hydrocarbon radical containing from 10 to 32 carbon atoms; n is an integer from 2 to 6; and the salt forming aliphatic carboxylic acid is from the group consisting of aliphatic monocarboxylic, aliphatic dicarboxylic, hydroxy aliphatic monocarboxylic and hydroxy aliphatic polycarboxylic acids containing 2 to 10 carbon atoms, said carboxylic acid containing only carbon, hydrogen and oxygen atoms, said salt being water dispersible to the extent of at least 5% by weight.

6. A process of inhibiting corrosion in steam and condensate return systems in which the steam and condensate are carried by ferrous metal pipes normally susceptible to corrosion which comprises introducing into such systems a corrosion inhibiting amount of an aliphatic carboxylic acid salt of an hydroethylation reaction product of from 1 to 4 mols of ethylene oxide per mol of an alkylene diamine of the formula



where R is a mixture of acyclic hydrocarbon radicals containing from 10 to 32 carbon atoms normally occurring in vegetable oils and fats; n is an integer from 2 to 3; and the salt forming aliphatic carboxylic acid is from the group consisting of aliphatic monocarboxylic, aliphatic dicarboxylic, hydroxy aliphatic monocarboxylic and hydroxy aliphatic polycarboxylic acids containing not more than 10 carbon atoms, said carboxylic acid containing only carbon, hydrogen and oxygen atoms, said salt being water dispersible to the extent of at least 5% by weight.

7. A process of inhibiting corrosion in steam and condensate return systems in which the steam and condensate are carried by ferrous metal pipes normally susceptible to corrosion which comprises introducing into such systems a corrosion inhibiting amount of at least 1 part per million of the acetic acid salt of the reaction product of 3 mols of ethylene oxide and one mol of N-tallow propylene diamine.

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COVER

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,029,125

April 10, 1962

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 8, line 51, for "2,126,174" read -- 2,126,173 --.

Signed and sealed this 25th day of September 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents