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(54) Composition and method for inhibiting corrosion in steam condensate systems.

(57) Use of methoxypropylamine as a neutralizing amine in combination with hydrazine to prevent corrosion in steam condensate systems or in other low solids aqueous systems.

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"COMPOSITION AND METHOD FOR INHIBITING CORROSION IN
STEAM CONDENSATE SYSTEMS"

BACKGROUND OF THE INVENTION

5 This invention relates to corrosion control in
steam condensate systems and other aqueous systems in
which the mineral content is relatively low.

More particularly, this invention relates to the
use of methoxypropylamine in combination with hydrazine
to control corrosion in steam condensate systems or in
10 other low solids aqueous systems.

Condensate corrosion protection is becoming an in-
creasingly important aspect of plant operation. In
these energy-conscious times, an increase in the quantity
and quality of condensate will result in water and heat
15 savings for the total boiler system.

Historically, the action of dissolved gases
such as oxygen and carbon dioxide have been two of

the main factors that lead to condensate corrosion. In order to understand the role of oxygen and carbon dioxide in corrosion, one must understand the electrochemical nature of corrosion. Pure water has very little effect on pure iron, but this situation is seldom encountered. Under most conditions, there is a tendency for iron to dissolve in water, and two electrons are released for each atom that dissolves. These electrons are transferred to hydrogen ions present in water, and the ions are reduced to elemental gaseous hydrogen. All action ceases at this point if the hydrogen remains on the surface of the metal since a protective coating is formed that interferes with the passage of electrons. However, any agent which increases the number of hydrogen ions present in the water, or which will cause the removal of the protective film, serves to increase the rate of corrosion.

When carbon dioxide dissolves, it reacts with water to form carbonic acid, which supplies additional active hydrogen to the system. Iron displaces the hydrogen from this acid. When oxygen is also present in the water, a two-fold reaction takes place. Some molecules of oxygen combine with the displaced hydrogen and thus exposes the metal to fresh attack. Other oxygen molecules combine with iron ions to form insoluble rust compounds.

A greater corroding influence than the mere dissolving tendency of iron is the existence of a heterogeneous surface in commercial iron and steel due to the presence of surface imperfections which tend to form couples with the adjacent base metal.

Electrons are released from the anodes of these couples to the hydrogen ions at the adjacent cathodic surface, thus increasing the corroding area and accelerating the rate of corrosion.

5 The first product of corrosion may be converted to ferric oxide, which is only loosely adherent and aggravates corrosion by blocking off areas to oxygen access. These areas become anodic and iron oxide
10 couples are set up. The iron under the oxide deposit then dissolves, and pitting develops. Carbon dioxide attack results in thinning or grooving of the metal.

 For those systems that will permit it, filming amines will give condensate corrosion protection against both oxygen and carbon dioxide. However,
15 many industrial systems cannot tolerate filming amines and must use neutralizing amines.

 The ideal neutralizing amine should have the following characteristics:

20 1. The distribution ratio should be high enough so that a considerable amount of the neutralizing amine fed to the boiler will end up in the condensate. This will reduce the loss of neutralizing amine via blowdown.

25 2. The distribution ratio should not be too high in order to keep losses due to aeration and venting to a minimum. The distribution ratio is the ratio of the amount of amine in the vapor phase to that in the liquid phase.

 3. The basicity value should be moderately

high or very high so that the amine will efficiently neutralize all carbon dioxide that it encounters.

4. The neutralizing amine should have sufficient hydrolytic-thermal stability so that it will not break
5 down to ammonia and other compounds in the boiler or in superheated or saturated steam.

5. The neutralizing amine should be a water-soluble liquid for feeding convenience.

Neutralizing amines such as cyclohexylamine and morpholine have been used but they have several disadvantages. For example, cyclohexylamine has a high
10 distribution ratio and accordingly, substantial cyclohexylamine escapes the system through the deaerator vent. Morpholine, on the other hand, has a low basicity value which means that more morpholine is required
15 to attain high pH's in the condensate system and it also has a very low distribution ratio which means that substantial amounts are lost via blowdown.

SUMMARY OF THE INVENTION

20 The neutralizing amine of this invention overcomes the above-mentioned disadvantages of cyclohexylamine and morpholine. Methoxypropylamine has a very desirable distribution ratio and a fairly high basicity value.

25 Methoxypropylamine may be used alone or in combination with an oxygen corrosion inhibitor such as hydrazine. In use, concentrations of 0.1 to 1000 mg/l, and preferably 1 to 100 mg/l, should be maintained in

the steam condensate system. When used in combination with hydrazine or another oxygen corrosion inhibitor, the compositions should contain on an active basis from about 1% to about 99% methoxypropylamine and from about 0.1% to about 50%, preferably about 1% to about 15%, of the oxygen corrosion inhibitor. The compositions of this invention may be fed to the steam condensate system being treated by conventional liquid feeding means or may be fed to the boiler feedwater or directly to the steam supply lines.

The following examples will illustrate the use of methoxypropylamine, alone and in combination with hydrazine, as a steam condensate corrosion inhibitor in accordance with the teachings of this invention.

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EXAMPLE 1

Distribution ratios of a number of neutralizing amines were calculated by preparing solutions of each amine having a concentration of 100 mg/l and adding 500 ml of this solution to a brine pot which is slowly and uniformly heated so that 100 ml of distillate is produced every 40 minutes. Additional solution is manually introduced to the brine pot every 5 to 10 minutes to maintain the brine pot solution at the 500 ml mark. Each 100 ml aliquot of distillate is collected and pH determined until constant pH is attained for three successive aliquots. This is taken to represent the establishment of equilibrium conditions. At equilibrium, the brine and the final 100 mls are analyzed by gas chromatography to determine the amount of amine in each and the Distribution Ratio (D.R.) calculated by the following

formula:

$$\text{D.R.} = \frac{\text{Amine Concentration in Final 100 mls}}{\text{Amine Concentration in Brine}}$$

Similarly, the basicity value (K_b) or measure of the amine's ability to react with carbon dioxide is calculated in accordance with the formula:

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}^0]}$$

wherein $[\text{BH}^+]$, $[\text{OH}^-]$ and $[\text{B}^0]$ are defined as:

$[\text{BH}^+]$ = concentration of dissociated amine
 $[\text{OH}^-]$ = hydroxide concentration
 $[\text{B}^0]$ = concentration of free, undissociated amine

The results of these tests and calculations are set forth in Table I.

Table I

15

Amine Properties

	<u>Molecular Weight</u>	<u>K_b</u>	<u>Distribution Ratio</u>
Cyclohexylamine	99	153×10^{-6}	3.8
Morpholine	87	2.4×10^{-6}	0.4
20 Diethylamino-ethanol	117	52×10^{-6}	2.7
2-amino, 2-methyl-propanol	89	40×10^{-6}	0.3
25 Methoxypropyl-amine	89	130×10^{-6}	1.0
Hydrazine	32	1.7×10^{-6}	---

EXAMPLE 2

The hydrolytic-thermal stability of various neutralizing amines is measured by a test in which the neutralizing amine at a concentration of 1000 mg/l is autoclaved for 24 hours at 600 psi (489°F) and the final concentration of ammonia measured. The results of this test are set forth in Table II.

Table II

	<u>Amine</u>	<u>mg/l NH₃</u>
10	Methoxypropylamine	< 1.0
	Morpholine	1.6
	Cyclohexylamine	3.3
	Diethylaminoethanol*	2.4
	Aminomethylpropanol	124.0

15 *Diethylaminoethanol breaks down appreciably to diethylamine.

EXAMPLE 3

A condensate test system is used to evaluate neutralizing amines. This system comprises a boiler capable of producing 45 kilograms/hour of a steam at pressure of 200 psi, pumps and metering devices to control the composition of the make-up water to the boiler, and cooling coils with temperature control means to condense the steam. The condensate is recirculated through a test loop where metal coupons and corrosometer probes evaluate the corrosion rate. The test water is distilled water containing <1 mg/l SO₄, <1 mg/l Cl, <1 mg/l SiO₂ and 10 mg/l CO₂. Table III sets forth the results of corrosion tests

in this system.

Table III

5	<u>Inhibitor</u>	<u>pH</u>	<u>Concentration</u>	<u>Corrosion Rate % Reduction from Control</u>
	Control	---	0	0%
	Cyclohexylamine	8.5	37.5 mg/l	48%
	Morpholine	8.5	152 mg/l	73%
	Methoxypropylamine	8.5	106 mg/l	75%

10

EXAMPLE 4

The condensate test system of EXAMPLE 3 was used to demonstrate the effect of the addition of hydrazine to methoxypropylamine in the inhibition of corrosion.

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Table IV

20	<u>Inhibitor</u>	<u>pH</u>	<u>Amount of Inhibition In System</u>	<u>Inhibition</u>	<u>Inhibition per ppm of Available Product</u>
	Control	---	-----	0%	0.00%
	MPA	8.5	106 ppm	75%	0.71%
	7% Hydrazine/ 93% MPA	8.5	61 ppm	83%	1.36%
25	15% Hydrazine/ 85% MPA	8.5	61 ppm	71%	1.16%
	Hydrazine	8.5	22 ppm	19%	0.86%
	1% Hydrazine/ 99% MPA	8.5	49.5 ppm	55%	1.11%

*MPA = Methoxypropylamine

WE CLAIM:

1. A steam condensate corrosion inhibiting composition consisting essentially of methoxypropylamine and hydrazine.
2. A steam condensate corrosion inhibiting composition of Claim 1 which contains from 1 to 15% by weight hydrazine.
3. A method of inhibiting corrosion in steam condensate systems which comprises maintaining an effective amount of a composition consisting essentially of methoxypropylamine and hydrazine.
4. A method of inhibiting corrosion in steam condensate systems as in Claim 3 wherein a concentration of at least 1.0 mg/l of said composition is maintained.
5. A method of inhibiting corrosion in steam condensate systems as in Claim 3 wherein the composition contains from 1 to 15% by weight hydrazine.

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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ⁷)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	<u>US - A - 3 983 048</u> (H.W. SCHIESSL) * Column 4, lines 45-68 * ---	1	C 23 F 11/14 C 02 B 1/10
	<u>LU - A - 36 675</u> (H.W. WINGS LACK-FABRIK) * Claims 1,3 * ---	1	
P	<u>FR - A - 2 359 909</u> (NALCO CHEM.CY) * Claims 1,7 * ---	1	
A	<u>US - A - 2 793 944</u> (J.A. CHENICEK) * Column 3, line 6 * ---		TECHNICAL FIELDS SEARCHED (Int.Cl. ⁷)
A	<u>US - A - 3 728 281</u> (C.E. MARKS) -----		C 23 F 11/10 11/14 C 02 B 1/10
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family, corresponding document
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 20-02-1979	Examiner VERHOEST