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2,890,928

CORROSION INHIBITION

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8 Claims. (Cl. 21-2.7)

The present invention relates to film-forming corrosion inhibitor compositions for use in steam condensate lines such as in boiler systems or selected portions of steam systems as in individual buildings which purchase steam from a general source for the purpose of providing effective corrosion protection in the liquid and also in the vapor phase by the introduction of very small quantities of the inhibiting composition in the system.

A commercially effective corrosion inhibitor composition for use in steam condensate lines must satisfy many rigid requirements. The inhibitor composition must be chemically stable at boiler temperatures for prolonged periods of time.

For the purpose of effective corrosion inhibition, the agent must be effective in the liquid and vapor states, effective in these states in small amounts, and the same agent used in the liquid phase must be carried from the liquid phase into the vapor stream by its vapor pressure and leave a reservoir of agent in the liquid phase.

Thus it should have a vapor pressure from water solution sufficient that the inhibitor composition will be carried by the steam to protect the portions of the steam condensate lines which are contacted by the steam without being quickly depleted from the liquid phase and so that the portions of the condensate lines contacted by liquid water will also be protected.

Further, the inhibitor composition should be readily and strongly adsorbed on the condensate lines to provide a compact molecular film which is not wet by water and which substantially precludes diffusion of water vapor, oxygen and carbon dioxide.

Desirably, the inhibitor composition should be readily dispersible in water at effective inhibiting concentrations and at the same time adhere strongly to metal surfaces such as the metal surfaces of steam pipes and the like of steam systems. The strongly adherent films of the inhibitor should resist leaching from these metal surfaces with respect to water condensing thereupon. It is also important that the inhibitor composition be inert with respect to the dissolved solids which may be present in the water.

In the United States patent to Morris E. Dreyfus, Number 2,053,024 dated September 1, 1936, it is taught that condensate lines can be protected against corrosion by dissolving in the boiler water certain alkaline amines which volatilize with the steam and condense with the condensate so that all parts of the system are retained in the protecting environment of the alkaline amine. Alkyl amines such as mono-amyl-amine and iso-amyl-amine are suggested. In use as the corrosion inhibitor, these amines are moderately to strongly alkaline and counteract acid components in the feed water.

The treatment of alkaline boiler water by high molecular weight amines such as saturated and/or unsaturated aliphatic amines for the purpose of reducing foaming is taught in the United States patent to Wayne L. Denman, No. 2,400,543, dated May 21, 1946 (Reissue Patent No.

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23,614). However, the higher molecular weight amines in the said Denman patent are also alkaline.

In the United States patent to Harry Lewis Kahler No. 2,460,259, dated January 25, 1949, it is indicated that high molecular weight amines form a substantial mono-molecular film on the surface of pipe lines and apparatus which reduces the corrosive action. Again, as in the aforesaid Dreyfus and Denman patents, the amines are alkaline.

It has now been discovered that small quantities of high molecular weight, primary aliphatic amides and alcohols, which are essentially neutral compounds, provide effective and lasting corrosion resistance in both the liquid and vapor phases.

It has further been found that small amounts of the amides provide exceptionally effective corrosion resistance in the vapor phase and that small amounts of the alcohols provide exceptionally effective corrosion resistance in the liquid phase.

It has also been discovered that when small amounts of the amides and alcohols are used together, that surprisingly effective corrosion resistance is provided both in the liquid and in the vapor phases, simultaneously.

The corrosion inhibitor compositions as above set forth are normally employed by introducing the inhibitor composition into the feed water. This is not essential, however, and the inhibitor composition may desirably be introduced under appropriate circumstances into the condensate or it may be sprayed or injected into the vapor phase, e.g., the steam. Thus, the inhibitor may be introduced directly into the steam line supplying a particular building or into the steam drum or steam header of a boiler plant.

Corrosion resistance in accordance with the invention can be effectively maintained by the utilization of at least 2 p.p.m., preferably about 10-100 p.p.m. and less than 500 p.p.m. of total inhibitor composition based on the total weight of water in the aqueous system involved. It will be understood that some of the inhibitor composition is in the liquid phase, some in the steam phase, and that some will be present in the system as a substantially mono-molecular film on those metal surfaces which are contacted by either the liquid water or the steam.

When the inhibitor composition is introduced into the feed water, less than 500 p.p.m. (normally from 20-50 p.p.m.) in the feed water is sufficient for the purposes of the invention.

To illustrate the effectiveness of the corrosion inhibitor compositions of the invention, these compositions have been tested and compared with a control of plain water and also compared with the use of an equal quantity of octadecyl amine acetate (a preferred high molecular weight amine falling within the teachings of the aforesaid patent to Kahler 2,462,259). It has been found that the inhibitor compositions in accordance with the invention are at least comparable in corrosion resistance with respect to preferred inhibitors as indicated in the aforesaid Kahler patent and as used in commerce at the present time. It has further been found that the amides of the invention provide superior vapor phase corrosion resistance and that the alcohols of the invention provide superior liquid phase corrosion resistance. It has also been found that the use of admixtures of amides and alcohols in accordance with the invention provides superior corrosion resistance in both the liquid and the vapor phases. Accordingly, the corrosion resistance which is achieved in accordance with the present invention in addition to equalling the best results which can be achieved using alkaline compositions as taught in Kahler, avoids the disadvantages inherent in alkaline materials. These new results are achieved by

employing essentially neutral compounds which are inert. Moreover, these results are achieved using the highly polar amides and alcohols instead of the amines. The inhibiting compositions of the invention adhere more strongly and permanently by virtue of their structure to the metal surfaces of the condensate lines than the amines and produce greater permanency of inhibition thereby.

The new corrosion inhibitor compositions of the present invention are inert and chemically stable on the forms of films which are particularly strongly absorbed to the surface of the condensate lines because of the strong polarity of the hydroxy and/or amide groups respectively. Without any intention of being limited to any particular theory, there is a distinct possibility that an interaction occurs between the hydroxy and the amide groups. As a result of the chemical inertness provided through the essentially neutral character of the amides and alcohols, and because of the enhanced polarity and adsorption on the condensate lines, the corrosion inhibitor films which are formed are long-lasting. Thus, the need to renew treatment of the feed water is substantially reduced. As a result, the feed water need be treated at less frequent intervals and this provides valuable economies as will be evident. Still further, and of considerable practical importance is the fact that corrosion resistance is now substantially independent of feed water pH, thereby obviating the need for precise chemical boiler water control which has been heretofore considered essential.

The high molecular weight primary aliphatic amides and alcohols in accordance with the invention have an aliphatic hydrocarbon radical containing at least 14 carbon atoms in the molecule.

In accordance with preferred practice of the invention, the aliphatic hydrocarbon radical is saturated and contains from 14 to 22 carbon atoms in the molecule and most preferably contains 18 carbon atoms in the molecule. The aliphatic hydrocarbon radical is preferably a straight-chain radical.

The corrosion inhibitor which serves to protect metal surfaces by introduction into the boiler feed water and volatilization with the distillate consists essentially of an essentially neutral high molecular weight compound selected from the group consisting of $C_nH_{2n+1}CH_2OH$ and $C_nH_{2n+1}CONH_2$ where n is an integer which equals 13 to 21 and mixtures of $C_nH_{2n+1}CH_2OH$ and



Particular preferred high molecular weight alcohols and amides are stearyl alcohol, palmityl alcohol, stearamide and palmitamide. The amides and alcohols of the following acids can also be used, myristic acid, arachidic acid, myristoleic acid, palmitoleic acid, oleic acid, linoleic acid, linolenic acid, elaeostearic acid, ricinoleic acid and licanic acid. These alcohols and amides can be used in admixture with one another. The saturated alcohols and amides are preferred, although these may contain minor proportions of the unsaturated alcohols and amides while retaining the characteristics of the saturated major components.

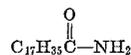
In the following tests, an attempt was made to determine the effectiveness of substances in reducing the corrosivity of steel. The apparatus employed was designed to test the corrosive effect which was observed in the liquid condensate, or in the liquid phase as well as in the vapor phase.

The apparatus employed consisted of 4 Soxhlet units. Each flask employed in the units contained 200 ml. of water containing 25 p.p.m. of corrosion inhibitor. Where a plurality of corrosion inhibitors were employed in admixture, equal parts of each inhibitor were used to provide a total concentration of 25 p.p.m.

The specimens tested were high carbon steel panels (the steel being SAE 1010) having a total surface area of approximately 4 square inches (panels 1" x 2").

Some of the panels were immersed in the liquid condensate portion of the Soxhlet unit and some were immersed in the vapor portion of the unit. Air was bubbled through the condensed liquid throughout the run. The temperature of the liquid condensate averaged about 80° C. The temperature in the vapor phase at atmospheric pressure was substantially 100° C. Thus, the liquid phase tests were run at 80° C. and the vapor phase tests were run at 100° C.

The steel test specimens defined above were cleaned by vapor degreasing with perchlorethylene and were rubbed with steel wool in perchlorethylene before each run. These specimens, at the completion of the test, were cleaned by soaking for 30 seconds in 10 percent dibasic ammonium citrate, followed by rinsing in alcohol and ether. The following were tested as corrosion inhibitors: n-octadecylamine acetate; a mixture of equal parts by weight of stearyl alcohol (commercial grade having a melting point of 49.53° C.); and stearamide of the formula



(a commercial mixture which is essentially neutral and substantially water insoluble having a melting point of approximately 98° C. and containing approximately 70% by weight of stearamide, approximately 25% by weight of palmitamide and about 5% by weight of unsaturated fatty amides primarily constituted by oleamide and palmitole amide). The amount of corrosion resulting from the test was measured by the weight loss suffered by the steel panels and was compared with a control of plain water.

The tests were run for a period of 40 hours and ten replicate tests were run in each instance to insure reliability of result.

With the water control, the steel panels lost about 0.010 gram when placed in the liquid phase and about 0.012 gram in the vapor phase. The use of octadecyl amine acetate in an amount of 25 p.p.m. showed significant improvement in corrosion resistance with respect to the water control. The averages of the replicates tested showed weight losses of about 0.005 to about 0.006 gram in the liquid phase. The results were not as good in the vapor phase and the weight loss was consistently higher than 0.006 gram although some appreciable improvement in corrosion resistance was still obtained. The mixture of equal parts of stearyl alcohol (commercial grade) and stearamide (commercial grade) when employed in a total amount of 25 p.p.m. again showed significant improvement in corrosion resistance with respect to the water control. The averages of the replicates tested showed weight losses of about 0.005 to about 0.006 in both the liquid phase and the water phase. This shows that the liquid phase results are fully comparable with the results achievable with octadecylamine and superiority of result in the vapor phase.

Further tests were made using stearyl alcohol alone and myristamide alone (each being used in an amount of 25 p.p.m.). The results of these further tests were not as consistent as when the two inhibitors were used together but there was demonstrated a significant improvement with respect to the water control. The tests also indicated the stearyl alcohol to be particularly good in preventing corrosion in the liquid phase whereas the myristamide was particularly effective in the liquid phase.

As will be appreciated, the use of the alcohol and the amide in admixture is of particular value in providing consistency of corrosion inhibition.

As previously indicated, the alcohols and amides of the invention are normally used by introducing them into the feed water. Since the alcohols and amides of high molecular weight aliphatic hydrocarbons are neither water-soluble nor water-dispersible, these compounds are preferably mixed with emulsifying agents to permit ready

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dispersion in the feed water. A preferred mixture using triethanolamine oleate as the emulsifying agent is as follows.

	Parts by weight
Stearyl alcohol (commercial grade, melting point 49-53° C.) -----	5.5
Stearic acid amide (commercial grade described here- inbefore) -----	5.5
Oleic acid -----	2.6
Triethanolamine -----	1.3
Water -----	85.1

In preparing the composition, the stearyl alcohol the stearic acid amide and the oleic acid are combined and heated to melt the mixture. The triethanolamine is dissolved in the water and heated to 85-90° C. The aqueous solution is then added slowly to the melted mixture of alcohol, amide and acid while agitating and the agitation is continued slowly while cooling to room temperature. The result is a paste which disperses readily in water and does not foam under normal conditions of boiler operation. This paste contains 11% corrosion inhibitor. The concentration of inhibitor can be increased by decreasing the water content, but this produces a firmer paste which disperses less readily. A preferred composition consists essentially of a mixture of stearylamine and stearyl alcohol, triethanolamine as an emulsifying agent and water as the dispersed phase, each of said stearylamine and stearyl alcohol being present in an amount of about 5.5%, said emulsifying agent being present in an amount of about 4% and said water being present in an amount of about 85% of said emulsion.

The preferred dispersion as set forth above is more readily dispersible than the amine inhibitor compositions which are presently available in commerce.

In addition to the effectiveness of corrosion resistance in both the liquid and vapor phases provided by the invention and the lasting and inert character of this protection, it is desired to point out that the alcohols and amides of the invention are less costly than the amines of the prior art. This provides an important economic advantage which should not be overlooked because of the importance of relative cost in commercial activities.

I claim:

1. The method of inhibiting corrosion of ferrous metal surfaces in a steam condensate system comprising adding to the boiler feed water a corrosion inhibitor volatilized with the distillate consisting essentially of an essentially neutral high molecular weight compound selected from the group consisting of $C_nH_{2n+1}CH_2OH$ and



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where n is an integer which equals 13 to 21 and mixtures of $C_nH_{2n+1}CH_2OH$ and $C_nH_{2n+1}CONH_2$.

2. The method recited in claim 1 in which said compound is stearyl alcohol.

3. The method recited in claim 1 in which said compound is stearamide.

4. The method recited in claim 1 in which there is added to said boiler feed water a mixture of stearyl alcohol and stearamide.

5. The method recited in claim 1 in which there is added to said boiler feed water a mixture of stearyl alcohol and a saturated primary amide containing 14 to 18 carbon atoms.

6. The method recited in claim 1 wherein said corrosion inhibitor is added to the boiler feed water in the form of an emulsion including a water soluble fatty acid soap as emulsifying agent.

7. The method as recited in claim 6 wherein said emulsion contains about equal proportions by weight of stearyl alcohol and stearyl amide, the total weight of said alcohol and amide being in an amount of from 2-500 parts per million by weight of the boiler feed water.

8. A water-dispersible corrosion inhibiting aqueous emulsion for protecting ferrous metals in a steam condensate line adapted to be added to boiler feed water and be volatilized with the distillate in said line, consisting essentially of a mixture of stearylamine and stearyl alcohol, triethanolamine as an emulsify agent and water as the dispersed phase, each of said stearylamine and stearyl alcohol being present in an amount of about 5.5%, said emulsifying agent being present in an amount of about 4% and said water being present in an amount of about 85% of said emulsion.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,890,928

June 16, 1959

Lloyd I. Osipow

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.

In the grant, line 1, and in the heading to the printed specification, line 3, name of inventor, for "Lloyd I. Osipowe", each occurrence, read -- Lloyd I. Osipow --.

Signed and sealed this 27th day of October 1959.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

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