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PREVENTION OF CORROSION IN STEAM GENERATION

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This invention relates to the art of treating water in boilers, steam generators, evaporators and the like, and the treatment of the steam and the condensate produced therefrom to reduce or prevent the corrosion of steam lines, traps, condensers and other pieces of equipment carrying the steam and the condensate. The invention also relates to the preparation of new and improved water treating compositions.

It is known that certain amines may be added to boiler water from which they will volatilize with the steam and condense and dissolve in the condensed steam to inhibit corrosion occurring in the condensate lines. These amines may also be added directly to the steam lines. The amines proposed for this purpose are liquids boiling within the range from 0 degrees C. to 171 degrees C. at atmospheric pressure. These liquid amines are, in general, highly caustic and present a serious hazard in their handling. Furthermore, they are quite volatile even under ordinary temperature conditions and the toxicity of their fumes in high concentrations presents a further hazard in their use. Moreover, the addition of liquids to a boiler or to the steam lines is attended with many mechanical and practical difficulties.

An object of the present invention is to provide a composition for the treatment of boiler water, steam and steam condensates, which composition is in a substantially dry form that is readily soluble or dispersible in water, and from which suitable amines are liberated by the action of alkaline boiler water.

Another object of the invention is to prepare corrosion inhibiting composition of the type described in the form of briquettes which are gradually and uniformly dissolved in the feed water to a steam boiler, evaporator or the like. Other objects will appear hereinafter.

In accomplishing these objects in accordance with the invention it has been found that corrosion inhibition in steam generating systems can be obtained by incorporating with the boiler feed water certain crystalline non-hygroscopic water soluble polyamine salts. These polyamine salts are solids which are capable of liberating the free amines when added to the feed water of a steam boiler containing sufficient alkali to decompose the amine salts into free amines at steam generating temperatures. These amine salts can also be incorporated with other water treating chemicals either by mixing them together to produce a dry, free flowing powder or by briquetting them with a suitable binder, preferably one which is water soluble. The preferred compositions consist of the amine salts briquetted with other water treating chemicals, e. g., tannins, lignin sulfonates, sodium sulfite, or the like, by means of binders such as dextrines.

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Assuming that the alkali added to the boiler water is sodium hydroxide, the general reaction which occurs between the amine salt and the alkali with the liberation of the amine may be described by the following equation:

Amine salt+NaOH (boiler water)→
Amine (volatile)+Na-salt (boiler water)

Generally speaking, the quantities of amine salt required for the purpose of the invention are so small that the quantities of alkali employed in the boiler water will be sufficient to react with the amine salt and liberate the free amine while still maintaining an alkaline condition in the boiler water. In some cases, however, where the amine salt is made up with an excess of acid or acid salt, it may be desirable to add larger amounts of alkali to the boiler feed water to compensate for the alkali which is utilized in the reaction with the amine salt. The quantity of alkali required for this purpose can readily be calculated by any one skilled in the art.

The polyamines which are useful for the preparation of amine salts in accordance with the practice of the invention should possess the following properties:

1. The polyamine should distill or volatilize with steam in appreciable quantities in the boiler pressure range of superatmospheric pressures from 5 to 250 pounds per square inch or at higher pressures if such pressures are employed.

2. The polyamine should not cause foaming and carryover.

3. It should not decompose appreciably under boiler conditions of alkalinity, pH, pressure and temperature.

4. The boiling point of the polyamine should preferably be above 100 degrees C. so that appreciable amounts of the amine are not lost in venting or preheating of the feed water and so most of the amine will be in the liquid phase in the portions of the system handling hot condensate. It should be pointed out that boiling point alone is not the factor which determines the relative volatility of the amine with steam, as the tendency to form stable hydrates and other factors also influence this behavior.

5. The polyamine should not form stable carbonic acid addition products which will not decompose to the amine and carbon dioxide at preheater temperatures.

6. The carbonic acid addition products of the polyamine should be reasonably water soluble.

7. The polyamine should have a low equivalent weight. The lower the weight of the amine for each neutralizing amino group the less the quantity of the amine required to inhibit corrosion in the steam system.

8. The polyamine should preferably be of a type which forms a protective film on the steam and condensate lines that will inhibit oxygen corrosion.

9. The polyamine should preferably have such vapor pressure characteristics that in boiling dilute aqueous solutions little change occurs in the water to amine ratio thus providing nearly constant alkalinity in the boiling water and the steam condensate.

Specific illustrations of suitable amines for most steam systems are ethylenediamine (b. p. 116 degrees C.) and diethylenetriamine (b. p. 206 degrees C.). These amines are miscible with water in all proportions.

The polyamine salts of mineral acids and organic carboxylic and/or sulfonic acids can be prepared by dissolving the acid in a solvent, e. g., water, diethyl ether or methanol, and adding the equivalent quantity of polyamine with stirring at a rate such as to avoid overheating. Cooling may be resorted to, in some cases. The salt is then recovered by filtration and, if necessary, evaporation. In cases where the corresponding amide is water insoluble care must be taken in the preparation of the salt to avoid dehydration to the amide. Another way in which the polyamine salts may be conveniently prepared consists in conducting the neutralization or partial neutralization of the polyamine in the presence of a solid material capable of absorbing the water of reaction, thereby yielding a dry appearing product without actually drying by evaporation. An example of this procedure is to mix the polyamine with a large excess of sodium acid sulfate either with or without the addition of anhydrous sodium sulfate. The amine will then be converted to a mixed amine salt, namely, sodium amine sulfate, and the water will be absorbed by the excess of salt or salts producing a dry appearing powder.

The following polyamine salts or mixed salts have been prepared and have been found to be suitable for the practice of the invention:

A. The hydrochloride, the hydrobromide, the nitrate, the sulfate, the orthophosphate, the pyrophosphate, the acetate and the 2-naphthalene sulfonate of ethylenediamine in the form of the neutral salts (i. e., with both amino groups neutralized).

B. The acid nitrate (one amino group neutralized) and the acid oxalate of ethylene diamine.

C. The nitrate, the hydrochloride, the sulfate, the orthophosphate, the acetate, the phenyl acetate and the 2-naphthalene sulfonate of diethylenetriamine as the neutral salts.

D. The mixed alkali metal amine neutral salts of ethylenediamine monosodium orthophosphate, and the mixed neutral salts of ethylenediamine lignin sulfonic acid and sulfuric acid.

The above mentioned amine salts are substantially non-hygroscopic solid water soluble salts, but it will be understood that not all polyamine salts have satisfactory properties for the purpose of the invention even though the amine itself may be suitable in other respects for inhibiting corrosion in a steam system. Thus, the phenyl acetate of ethylenediamine was too hygroscopic to be isolated.

The following examples are given to show methods of preparing polyamine salts suitable for the practice of the invention and also to illustrate the preparation of compositions containing such salts, it being understood, however, that these examples are not intended to limit the scope of the invention.

Example I

Ten (10) parts by weight of diethylenetriamine and 90 parts by weight of nitre cake were thoroughly mixed in a putty chaser type of mixer until only slightly damp. Upon standing a short time this slightly damp mass further reacted to become dry, whereupon it was ground to give a powder, readily water soluble, and containing 10% amine in the form of the sodium and diethylenetriamine mixed sulfate.

Example II

In a putty chaser 35 parts by weight of the monohydrate of monosodium orthophosphate and 5 parts by weight of diethylenetriamine were thoroughly mixed after which 10 parts of dextrin and about 1 part of water (parts by weight) were added and the mixture briquetted. The briquettes were dry and non-sticky, and readily dissolved in water. The amine salt formed was the sodium and diethylenetriamine mixed phosphate.

Example III

In a putty chaser 24 parts of monohydrate of monosodium orthophosphate, 11.5 parts ground nitre cake, and 7.5 parts of diethylenetriamine were thoroughly mixed after which 5 parts dextrin and 2 parts water were added and the mixture briquetted. The resulting briquettes were very hard and dry, and readily water soluble. The amine salts were a mixture of the salts which occur in Examples I and II.

Example IV

Fifty (50) parts of monohydrate of monosodium orthophosphate, 24 parts of sodium bisulfite, and 15 parts of diethylenetriamine were mixed after which 7 parts of dextrin and 4 parts of water were added and the mixture briquetted. The amine salt formed was mainly the sodium and diethylenetriamine mixed phosphate.

In the following examples, V to VII, inclusive, the procedure of mixing was substantially the same as in the Examples I to IV, inclusive. The materials shown were made into briquettes.

Example V

	Parts by weight
Monosodium orthophosphate, anhydr.	18
Diethylenetriamine	3.75
Dextrin	2.25
Water	2.0

Example VI

	Per cent
Monohydrate of monosodium orthophosphate	60
Sodium bisulfite	12
Dextrin	9
Diethylenetriamine	15
Water	4

Example VII

A dry powder was made up from lignin sulfonic acid, ethylenediamine, and sulfuric acid to give a product having the following analysis:

	Per cent
Sulfate of ethylenediamine	45.5
Sulfonate of the diamine	4.6
Total SO_3 content	6.1
Lignin organic matter	42.9

This neutral salt material was then used in a steam system to inhibit steam corrosion.

As previously stated, in order to introduce the amine salt into the steam system it is preferable to prepare it in the form of a briquette with other water treating chemicals and to cause it to be dissolved uniformly and gradually by the feed water to the boiler. This is conveniently accomplished by preparing the briquette and introducing it into a by-pass feeder which is connected in the boiler feed water line. The boiler feed water circulates through the feeder gradually dissolving the briquette and carrying the amine salt into the boiler where the amine is liberated by the action of the heat and inorganic alkali present. The liberated amine is then preferably volatilized at a uniform rate such that little change occurs in the water to amine ratio. The manner in which the amine volatilizes will, of course, depend upon the chemical and physical characteristics of the amine. The volatilized amine should serve to provide a nearly constant alkalinity in the boiling water and should redissolve in the steam condensate to provide the desired alkalinity in the latter at the point where condensation occurs.

The quantity of the amine salt initially added to the water from which the steam is generated should preferably be approximately 0.015 pound for each neutralizing amino group per grain of methyl orange alkalinity per thousand gallons of water. This means that if the methyl orange alkalinity of the feed water were 10 the quantity of amine salt would be that quantity capable of liberating 0.15 pound of said amine per thousand gallons of feed water. If the methyl orange alkalinity were 20 the recommended dosage of amine salt would be the equivalent of 0.30 pound of said amine per thousand gallons of water. In a similar manner the dosage can be calculated for waters of different alkalinities. These dosages are based upon a pressure of 250 p. s. i. and the corresponding steam temperatures with adequate venting of the preheater.

The dosage can also be established by observation of the pH obtained in the condensate. In general, it is preferable to maintain a pH in the steam condensate of about 7.0, although it has been observed that substantial corrosion protection has been obtained at a lower pH, as low as 6.3. The preferred pH range in the steam condensate is about 6.5 to about 7.5.

The treatment described herein can be employed in steam generation where the steam generators are operated at operating pressures from a high vacuum to rather high superatmospheric pressures. It will be understood, however, that of the amines suggested some would be better than others for different pressure operations.

Having thus described the invention, what I claim as new and desire to secure by Letters Patent of the United States is:

1. In a process of generating steam, the method which comprises generating steam from an alkaline boiler water while incorporating into the feed water to the boiler a quantity of a polyamine salt from the group consisting of the neutral hydrochloride, hydrobromide, nitrate, orthophosphate, pyrophosphate, acetate, and 2-naphthalene sulfonate of ethylenediamine, the acid nitrate and acid oxalate of ethylenediamine, the mixed alkali metal amine neutral salts of ethylenediamine monosodium orthophosphate, the mixed neutral salts of ethylenediamine lignin sulfonic acid and sulfuric acid, the nitrate, the sulfate, the orthophosphate, the hydrochloride, the acetate, the phenyl acetate and the 2-naphthalene sulfonate of diethylenetriamine as the neutral salts, the quantity of alkali in the alkaline boiler water being in excess of the amount required to hydrolyze said salt and the quantity of the salt being effective to liberate a corrosion inhibiting quantity of the polyamine upon said hydrolysis and being equivalent to approximately 0.015 pound for each neutralizing amino group in the amine per grain of methyl orange alkalinity per thousand gallons of water.

2. In a process of generating steam, the method which comprises generating steam from an alkaline boiler water while incorporating into the feed water to the boiler a quantity of a polyamine salt from the group consisting of the neutral hydrochloride, hydrobromide, nitrate, orthophosphate, pyrophosphate, acetate, and 2-naphthalene sulfonate of ethylenediamine, the acid nitrate and acid oxalate of ethylenediamine, the mixed alkali metal amine neutral salts of ethylenediamine monosodium orthophosphate, the mixed neutral salts of ethylenediamine lignin sulfonic acid and sulfuric acid, the nitrate, the sulfate, the orthophosphate, the hydrochloride, the acetate, the phenyl acetate and the 2-naphthalene sulfonate of diethylenetriamine as the neutral salts, the quantity of alkali in the alkaline boiler water being in excess of the amount required to hydrolyze said salt and the quantity of the salt being effective to liberate a corrosion inhibiting quantity of the polyamine upon said hydrolysis and to maintain a pH in the condensate of at least 6.3.

3. In a process of generating steam, the method which comprises generating steam from an alkaline boiler water while incorporating into the feed water to the boiler a quantity of a polyamine salt from the group consisting of the neutral hydrochloride, hydrobromide, nitrate, orthophosphate, pyrophosphate, acetate, and 2-naphthalene sulfonate of ethylenediamine, the acid nitrate and acid oxalate of ethylenediamine, the mixed alkali metal amine neutral salts of ethylenediamine monosodium orthophosphate, the mixed neutral salts of ethylenediamine lignin sulfonic acid and sulfuric acid, the nitrate, the sulfate, the orthophosphate, the hydrochloride, the acetate, the phenyl acetate and the 2-naphthalene sulfonate of diethylenetriamine as the neutral salts, the quantity of alkali in the alkaline boiler water being in excess of the amount required to hydrolyze said salt and the quantity of the salt being effective to liberate a corrosion inhibiting quantity of the polyamine upon said hydrolysis and to produce a pH in the steam condensate within the range of about 6.5 to about 7.5.

4. In a process of generating steam and of condensing the steam so as to protect against corrosion metal parts of the system where the steam is condensed, the method which comprises incorporating into boiler feed water from which the steam is generated and which contains an alkali, a quantity of a neutral sulfate of diethylenetriamine, the quantity of alkali in said boiler water being in excess of the amount required to hydrolyze said sulfate to free the diethylenetri-

amine and the quantity of said sulfate being effective to liberate a corrosion inhibiting quantity of diethylenetriamine and to produce a pH in the steam condensate of at least 6.3.

5. In a process of generating steam and of condensing the steam so as to protect against corrosion metal parts of the system where the steam is condensed, the method which comprises incorporating into boiler feed water from which the steam is generated and which contains an alkali, a quantity of a neutral phosphate of diethylenetriamine, the quantity of alkali in said boiler water being in excess of the amount required to hydrolyze said phosphate to free the diethylenetriamine and the quantity of said phosphate being effective to liberate a corrosion inhibiting quantity of diethylenetriamine and to produce a pH in the steam condensate of at least 6.3.

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