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TREATMENT OF STEAM SYSTEMS

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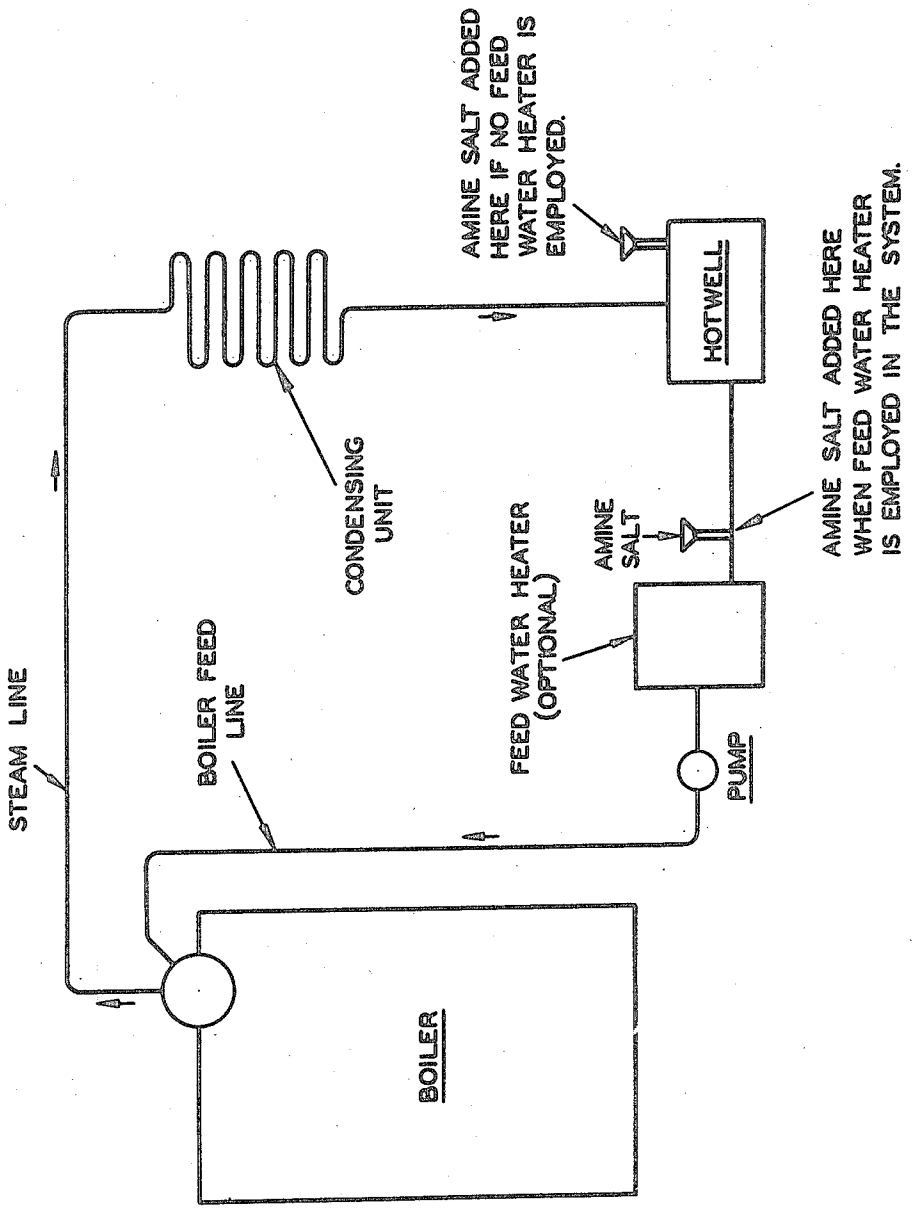

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TREATMENT OF STEAM SYSTEMS

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This invention relates to a method of preventing or retarding corrosion of steam systems.

More specifically stated, the invention relates to a method of preventing, inhibiting, or retarding corrosion of metallic surfaces coming in contact with steam vapor or condensate in such systems.

The deterioration of metallic surfaces in a steam system is greatly accelerated by acidic conditions and/or the presence of oxygen. Acidic corrosion in the boiler is easily eliminated by alkali treatment of the boiler feed-water, but this does not insure the absence of acidic corrosion in the condensate system which is caused by dissolved carbon dioxide. Carbon dioxide enters the system in several different ways. Since it is a constituent of air, any air entering the system brings with it a certain amount of carbon dioxide. Carbon dioxide is dissolved in the make-up water which is added to the system. It is also a decomposition product of carbonates and bicarbonates present in the boiler water. The water employed in steam systems also often contains dissolved oxygen. When the water is heated to form steam, the dissolved oxygen is released from the water and mixes with the steam. Oxygen also may enter steam systems by in-leakage when the internal pressure is less than that of the atmosphere. When the steam contains a mixture of dissolved oxygen and carbon dioxide, this combination becomes extremely corrosive as the steam condenses on metal surfaces.

Generally stated, an object of this invention is to provide a method of treatment whereby the steam may be permeated with a volatilized amine to render the steam condensate materially less corrosive than it would otherwise be, and under optimum conditions to make such condensate non-corrosive.

More specifically, it is an object of this invention to provide a process whereby acid-reacting water soluble salts of certain amines may be introduced at some appropriate place into a steam system, preferably near the terminal of the condensate return line, or between such terminal and the boiler.

Other objects of the invention and the manner of practicing the same will be apparent from the following description taken in conjunction with the single figure in the drawing, in which a steam system is diagrammatically illustrated with legends to indicate the various parts thereof.

It is common practice to treat boiler water with alkaline materials such as caustic soda, and

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consequently there is little likelihood of acidic corrosion in the boiler. However, the alkaline alkali-metal salts and hydroxides do not as a rule carry over with the steam if the boiler is operated efficiently. Therefore, that part of the system which is in contact with condensate from the steam does not receive the benefit of the alkaline compound which has been added to the boiler and may be exposed to acidic conditions. Corrosion, accordingly, may occur in the steam line, the condenser, and the condensate return lines, unless preventive steps are taken. Dreyfus in U. S. Patent 2,053,024 discloses the use of certain water-soluble alkaline volatile amines which have been found effective in preventing or reducing acidic corrosion by steam condensate in those parts of the system which have been mentioned. In practicing this invention, the amine is dissolved in the boiler water, volatilized with the steam and condensed with the condensate so that an alkaline environment is maintained in all parts of the system. Upon leaving the boiler, the volatile amine reacts with carbon dioxide and carbonic acid to form both amine carbonates and amine bicarbonates. If a slight excess of amine beyond that amount required to neutralize the acidic compounds is carried into the condenser, some free amine in an uncombined state will flow through the system.

Generally speaking, most of the commercially available volatile amines which are used in practicing the Dreyfus invention are relatively difficult to handle inasmuch as their vapors are extremely pungent and obnoxious, and if any of these particular amines come in contact with the human skin considerable irritation is observed. The storage and handling of the volatile amines are matters which require care since the materials are inflammable. The salts of the volatile amines, which I employ, are free-flowing solids rather than liquids, consequently they have very low vapor pressures and have practically no odor. In addition, they present no fire hazard, are easily handled, and if they should come in contact with the skin, no appreciable injury is done.

In most cases, some part of the steam system between the terminal of the condensate return line and the boiler is open to the atmosphere. The condensate may discharge into an open sump or hot-well, or a de-aerating or open feed-water heater may be installed for the dual purpose of removing air from the system and heating the feed-water before it enters the boiler. Since both the amine bicarbonate and amine car-

bonate are fairly unstable, it is not unusual to find that in passing through a hot-well, or de-aerating heater they are decomposed into free amine and free carbon dioxide. A considerable portion of any uncombined amine may thereby escape from the system through such an opening under these conditions. Although it is extremely desirable to remove as much carbon dioxide from the system as possible, the loss of volatile amine is undesirable as it should be retained for re-combination with additional carbon dioxide which subsequently enters the system.

In accordance with the process of my invention, an acid-reacting amine salt is added to the system at any convenient point between the terminal of the condensate return line and the boiler. Where a de-aerating heater is installed ahead of the boiler, the addition should be made to the water as it enters the heater or at some convenient point in the condensate return line preceding the heater. Inasmuch as the pH values of the various amine salts used in practicing this invention are within the range of from 1–6, it is desirable that these acid-reacting materials be added to the water as close to the heater as possible so that only a small section of the condensate return line is exposed to lowered pH values. To mitigate corrosion by the amine salts in this part of the steam system, any one of several phosphates can be added in an amount ranging from 1–10 P. P. M. as is well known in the art of water treating. If a heater is not installed in the system, addition of the amine salt can be made conveniently at the sump or hot-well into which the condensate return water is discharged.

The single figure of the drawing with its legends illustrates the application of the process as above described.

By using the amine salts, the amine is introduced into the system and at the same time, since the salts are acid-reacting, they assist in the liberation of carbon dioxide from the amine carbonates and amine bicarbonates in the condensate. Although salts at the upper end of the pH range 1–6 will not assist in liberating carbon dioxide as effectively as will the more acidic salts, smaller amounts of strong base would be required in the boiler to maintain proper alkalinity of the boiler water. In the table, I enumerate the various stages through which the amine passes in a steam system to which I have added certain amine salts.

Table

1. Addition of amine salt at hot-well, sump, feed water heater, or other suitable place:
   Amine salt is added to the system, lowering the pH and facilitating loss of carbon dioxide from the condensate.
2. Boiler:
   Water vaporizes to steam.
   Bicarbonates and carbonates are hydrolyzed producing CO_2 which passes off in steam leaving residual alkalinity in boiler water.
   Amine salt reacts with strong base present in boiler to produce free amine and alkali-metal salt, thereby proportionately reducing the alkalinity of the boiler water. Amine is volatilized and mixes with steam while the alkali-metal salt remains in the boiler.
3. Steam line:
   Steam containing admixed carbon dioxide and amine passes to condensing unit.
4. Condensing zone:
   Steam condenses to water.
   CO_2 and amine dissolve in water, amine neutralizing to the extent present the acidity produced by CO_2.
5. Further addition of amine salt as in step 1:
   Amine salt has acid reaction thereby assists in liberation of CO_2 from the amine carbonates and bicarbonates formed in the system. Also, as the salt is added, make-up of potential amine is provided to replenish what little amine is lost from the system.

In treating steam systems with a volatile alkaline amine to reduce acidic corrosion, it is general practice to add sufficient amine to raise the pH value of the condensate water to a range of from about 6.0 to about 8.3. Higher pH values may be maintained, if necessary, by adding increased quantities of amine. The pH value may be determined by the use of phenolphthalein or some other suitable indicator added to samples of condensate. The greater the amount of acid-reacting amine salt added to the system and reacted with alkali in the boiler to liberate amine, the greater will be the pH value of the condensate.

Having introduced an amine salt into the system, subsequent additions of amine salt are required for a two-fold purpose: to assist in the liberation of CO_2 from the system and to replenish what amine may be lost from the system. The amount of amine salt required will be governed by the concentration of free amine necessary for protection against corrosion in the condensing zone of the system. Since the amine carbonates and bicarbonates, which are formed in this zone when the free amine reacts with the carbonic acid and carbon dioxide present in the steam, are relatively unstable at feed-water heater temperatures, some amine and some carbon dioxide will be lost to the atmosphere. If small amounts of the acid-reacting amine salt are added to replenish the loss of amine, the pH of the condensate will be lowered with a consequent increase in the partial pressure of the carbon dioxide together with a decrease in the partial pressure of the amine.

The continuous feed of a very small amount of amine salt solution prevents the loss of excessive amounts of free amine, promotes the liberation of carbon dioxide and continuously introduces a small amount of potential amine to maintain the desired pH value in the condensate. If the continuous feed of amine salt is not desired, the salt may be fed intermittently when the concentration of amine in the condensing zone becomes too low for effective corrosion protection.

I may employ a water-soluble salt of any one of a large number of amines in practicing my invention. For effective inhibition of corrosion in the condensing zone of the steam system the amine must be sufficiently alkaline to neutralize the acidity present and it must be sufficiently volatile so that it will not remain in the boiler but will pass over with the steam into the condensing zone. A suitable measure of alkalinity is the dissociation constant. Amines having a constant of at least 1×10^{-6} are effective.

The salt of any suitable alkaline amine may be used if that amine is made available to those parts of the system susceptible to corrosion by the condensing steam. At a temperature of 100° C. prevailing in a boiler at atmospheric pressure, any amine boiling at 100° C. or less

would rapidly volatilize and pass out of the boiler. Salts of the following amines whose boiling points are less than 100° C. are typical of the compounds I may use: (figures indicate boiling points at atmospheric pressure) trimethylamine 3.5° C., isopropylamine 33° C., triethylamine 89.5° C., and isoamylamine 95° C. I may also use salts of amines boiling at temperatures of less than 0° C.

Many amines having boiling points in excess of that of water at atmospheric pressure may be used to prevent corrosion in steam systems. A number of amines having a high boiling point exhibit a sufficient vapor pressure to distill with the steam so that salts of amines boiling even at temperatures greatly in excess of 100° C. may be used in practicing my invention. For example, tripropylamine boils at 156° C., trimethylenediamine at 135° C., morpholine at 128° C., cyclohexylamine at 134° C., and monoethanolamine at 171° C. The water-soluble salts of any of these amines may be employed in my process since the amines which are liberated from the salt by the alkalinity of the boiler will distill with the steam in effective amount and at a sufficiently rapid rate to protect the condenser and the condensate return lines from acidic corrosion.

It should be understood that I may use the water-soluble salt of any alkaline amine which at the temperatures and pressures encountered will pass from the boiler to the condensing zone of the steam system in sufficient concentration to reduce or prevent acidic corrosion. I do not limit myself to salts of amines boiling in a specified range but include salts of amines which are effective under the conditions observed in the operation of a steam system.

The sulfates, sulfites, bisulfates, bisulfites, phosphates, phosphites, nitrates, and hydrochlorides are the preferred salts I employ in treating steam systems. By the term phosphates, I mean to include both the crystalline phosphates such as orthophosphates, pyrophosphates, and tripolyphosphates, and the amorphous phosphates commonly referred to as phosphate glasses. By reacting equivalent weights of amine and acid, the salt is formed. It may be wise under certain conditions to select a particular salt the anion of which has properties desirable in water treating. For example, an amine phosphate would assist in preventing scale formation while an amine nitrate would be useful in preventing embrittlement of the boiler steel. An amine sulfite would inhibit attack of the boiler by dissolved oxygen. In each of these instances, the amine would be liberated by the alkalinity of the boiler water and would pass over to the condensing zone of the system.

Having thus described my invention, what I claim as new and desire to secure by Letters Patent is:

1. In the process of preventing corrosion in the condensing zone of a closed condensate return steam system provided with a boiler for supplying steam thereto wherein a strong base substance is maintained, by means of a volatile alkaline amine, that step which comprises introducing into the system at a point between the terminal of the condensate return line and the boiler a water-soluble acid-reacting salt of an amine which amine has a dissociation constant of at least 1×10^{-6}, thereby promoting the liberation of carbon dioxide from the return condensate water and reducing the loss of free amine from the system.

2. The method of treating a steam system having mechanical means by which gaseous substances in said system may be evolved to inhibit corrosion in the condensing zone thereof which comprises introducing into the system at any suitable point between the condensing zone and the evaporating zone thereof a water-soluble, acid-reacting salt of a volatile amine, said amine having a dissociation constant of at least 1×10^{-6} maintaining a strong base substance in the evaporating zone of the system, passing said acid-reacting salt into the evaporating zone where it reacts with said strong base to liberate the volatile amine, circulating said amine through the condensing zone of the system whereby carbonates and bicarbonates of the amine are formed, adding from time to time additional acid-reacting salt of the volatile amine whereby carbon dioxide is liberated and loss of the amine is minimized, and passing the acid-reacting amine salt to the evaporating zone.

3. The method of treating a steam system having mechanical means by which gaseous substances in said system may be evolved to inhibit corrosion in the condensing zone thereof which comprises introducing into the system at any suitable point between the condensing zone and the evaporating zone thereof a water-soluble acid-reacting salt of a volatile alkaline amine, said amine being sufficiently alkaline to reduce acidic corrosion in the condensing zone of the system maintaining a strong base substance in the evaporating zone of the system, passing said acid-reacting salt into the evaporating zone where it reacts with said strong base to liberate the volatile amine, circulating said amine through the condensing zone of the system whereby carbonates and bicarbonates of the amine are formed, adding from time to time additional acid-reacting salt of the volatile amine whereby carbon dioxide is liberated and loss of the amine is minimized and passing the acid-reacting amine salt to the evaporating zone.

4. The method of inhibiting corrosion in the condensing zone of a steam system having mechanical means by which gaseous substances in said system may be evolved which comprises introducing into the system at any suitable point between the condensing zone and the evaporating zone thereof a water-soluble sulfite of a volatile alkaline amine, said amine having a dissociation constant of at least 1×10^{-6} maintaining a strong base substance in the evaporating zone of the system, passing said amine sulfite into the evaporating zone where it reacts with said strong base to liberate the volatile amine, circulating said amine through the condensing zone of the system whereby carbonates and bicarbonates of the amine are formed, adding from time to time additional amine sulfite whereby carbon dioxide is liberated and loss of the amine is minimized and passing the amine sulfite to the evaporating zone.

5. The method of inhibiting corrosion in the condensing zone of a steam system having mechanical means by which gaseous substances in said system may be evolved which comprises introducing into the system at any suitable point between the condensing zone and the evaporating zone thereof cyclohexylamine sulfite maintaining a strong base substance in the evaporating zone of the system, passing said cyclohexylamine sulfite into the evaporating zone where it reacts with said strong base to liberate

the volatile amine, circulating said amine through the condensing zone of the system whereby carbonates and bicarbonates of the amine are formed, adding from time to time additional cyclohexylamine sulfite whereby carbon dioxide is liberated and loss of the amine is minimized and passing the cyclohexylamine sulfite to the evaporating zone.

6. As an improved method of introducing a water-soluble volatile alkaline amine into a steam system having mechanical means by which gaseous substances in said system may be evolved whereby corrosion in the condensing zone thereof is reduced, the addition to the system at an appropriate point between the condensing zone and the boiler of a water-soluble, acid-reacting salt of the amine maintaining a strong base substance in the evaporating zone of the system, passing said acid-reacting salt into the evaporating zone where it reacts with said strong base to liberate the volatile amine, circulating said amine through the condensing zone of the system whereby carbonates and bicarbonates of the amine are formed, adding from time to time additional acid-reacting salt of the volatile

amine whereby carbon dioxide is liberated and loss of the amine is minimized and passing the acid-reacting amine salt to the evaporating zone.

7. The method as described in claim 6 where the acid-reacting amine salt is a salt of cyclohexylamine.

8. The method as described in claim 6 where the acid-reacting salt is the sulfite of an amine.

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