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⑤④ **Corrosion control composition and method for boiler/condensate aqueous systems.**

⑤⑦ A method of controlling corrosion in boiler/condensate aqueous systems which comprises adding to the system an amount of at least one volatile, flammable, relatively low molecular weight amine by feeding to the system at least one, less volatile, relatively high molecular weight amine which when subjected to conditions of temperature and pressure in the system partially decomposes into the at least one relatively low molecular weight amine.

A corrosion control additive for boiler/condensate aqueous systems which comprises an amount of a mixture of amines of varying relative molecular weights, volatilities and flammabilities, the mixture including at least one relatively high molecular weight amine and the relatively low molecular weight decomposition products thereof.

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CORROSION CONTROL COMPOSITION AND METHOD FOR BOILER/CONDENSATE AQUEOUS SYSTEMS

The present invention relates to compositions and methods for controlling the metal loss in boiler/condensate steam systems.

Iron and copper corrosion in steam condensate systems results in damage to piping and equipment as well as the loss of high quality water and energy. The corrosion products and process chemicals if returned to the boiler can contribute to the formation of damaging boiler deposits thereby reducing the reliability of the overall system and increasing operating and maintenance costs.

Iron corrodes in water in the absence of oxygen because iron is less noble than hydrogen. In pure water the ferrous hydroxide ($\text{Fe}(\text{OH})_2$) formed by iron and water elevates the pH by providing hydroxide ions and ferrous ions. This reduces the amount of hydrogen ion which tends to retard corrosion. If the water temperature rises, ferrous hydroxide is converted to magnetite (Fe_3O_4) in the absence of oxygen to form a somewhat protective film barrier. At temperatures of over 49°C (120°F), magnetite is formed based upon the overall reaction: $3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$.

Thus under laboratory conditions the corrosion of iron is self limiting. For actual condensate systems however, the presence of contaminants such as, for example, dissolved oxygen and carbon dioxide promote the corrosion reaction. In the presence of oxygen, ferrous hydroxide is unstable and ferric hydroxide is formed. Ferric hydroxide is not a corrosion reaction inhibitor as is ferrous hydroxide. Therefore, the presence of free oxygen in a given system enhances the corrosion reaction.

In addition to iron corrosion in water which is augmented by the presence of oxygen, corrosion of copper by oxygen may also occur. Generally, the resulting formation of cupric oxide is self limiting. If, however, copper complexing agents such as, for example, ammonia are present, the copper oxide film cannot become permanently established. High concentrations of carbon dioxide in the condensate system, at lower pH values (less than 8), have an effect similar to ammonia in dissolving the copper oxide film.

Carbon dioxide that dissolves in water causes the pH to be depressed and results in the formation of carbonic acid. Carbonic acid promotes the iron corrosion reaction by supplying the reactant H^+ . The overall reaction is: $2\text{H}_2\text{CO}_3 + \text{Fe} \rightarrow \text{Fe}(\text{HCO}_3)_2 + \text{H}_2$. The ferrous bicarbonate is soluble under many conditions and can act as a corrosion reaction retardant. The stability of ferrous bicarbonate in solution is effected by heat, pH and the partial pressure of carbon dioxide above the condensate. Often, these conditions change from location to location within the boiler/condensate system.

In the boiler, sodium carbonate and sodium bicarbonate react with heat plus water to form sodium hydroxide and carbon dioxide. Various external makeup water treatment methods can reduce the potential for carbon dioxide corrosion by lowering the alkalinity of the makeup water.

Due to the aqueous solubility of carbon dioxide, ground waters and surface waters contain carbonates among other dissolved solids. When these waters are heated in steam generating systems, the solubility of carbon dioxide decreases and the gas enters the produced steam. Upon condensation, carbon dioxide again dissolves to form carbonates. Since the condensate contains relatively few dissolved solids and thus little buffering capacity, the weakly acidic carbonate species can drastically lower the condensate pH. In turn, when acidic condensate mixes with makeup water, the steam generator feedwater pH can also decrease.

Carbonate containing waters cause acidic or general corrosion of the iron and copper metallurgies found in condensate and feedwater systems. This type of corrosion is evidenced by a general wastage or by gouging or pitting of the metal surface. If untreated, corrosion can cause failure of condensate return lines, feedwater piping, and other equipment (condensate receivers, pumps, heaters, etc.) associated with steam generator and hot water heating systems.

Several methods have been devised to control acid induced corrosion in these systems. Materials can be added that adsorb to the metal surface to form a thin barrier between the metal and the acidic solution. Examples of effective barrier-forming materials that are routinely used are long chain amines, such as, for example, octadecylamine; and axoles, such as, for example, tolyltriazole.

A second, more often utilized method of controlling carbonate-caused corrosion is the addition of amines to neutralize the carbonate and thereby increase the aqueous pH. Many different amines are utilized, but some commonly used materials include cyclohexylamine, morpholine, and methoxypropylamine. On an equal weight basis, the most effective amines are those that possess high basicity and low molecular weight. The high basicity allows attainment of high pH after acid neutralization, and low molecular weight allows greater molar concentrations (and thus more neutralization).

The addition of neutralizing amines neutralizes the acid (H^+) generated by the solution of carbon dioxide in condensate. The amines hydrolyze in water to generate hydroxide ions required for neutralization.

By regulating the neutralizing amine feed rate, the condensate pH can be elevated to within a desired range (e.g. 8.5 to 9.01). Numerous amines can be used for condensate pH neutralization and elevation. The selection of the appropriate amine is currently controlled by the basicity, stability and distribution ratio characteristics of the particular amine. The distribution ratio (DR) of an amine is expressed as formula DR
 5 equal to amine in vapour phase divided by amine in water phase (condensate) at some defined pressure or temperature.

Amines with a distribution ratio greater than 1.0 have more amine in the vapour phase than the water phase. The distribution ratio is a function of the pressure and the temperature in a boiler/condensate system to be treated. Distribution ratios (at atmospheric pressure) for commonly used neutralizing amines are as
 10 follows: Morpholine 0.4; diethylaminoethanol 1.7; dimethylisopropanol amine 1.7; cyclohexylamine 4.0; ammonia 10.0. The varying distribution ratios of commonly used neutralizing amines affect the loss of the amine from the system as well as the area in the system where the amine is most effective. Amines that have low distribution ratios provide excellent pH control at initial condensation sites, but poor neutralization at the final condensation sites. On the other hand, high DR amines are more likely to be found in remote
 15 sites in steam that has been in contact with the liquid phase as it passes through the steam distribution system.

In boiler/condensate systems where the bulk of the steam produced is used for turbine supply, morpholine is most suitable or a blend having a high morpholine content. The low DR for morpholine means that morpholine will be present in the initial condensate formed at the wet end of the turbine. In plants with
 20 extensive runs of steam lines, a material with a high DR is more desirable. In practice, the best protection is typically provided by a blend of amine products containing a variety of materials with differing distribution ratios.

Typical neutralizing amines have DR's from 0.1 to 10, but carbon dioxide has a DR of 100 or more depending upon temperature. Because of this difference in DR's, amines tend to concentrate in the
 25 condensate lines closest to the system boiler whereas carbon dioxide tends to concentrate in more remote areas of the condensate return system. Thus, conventional amine addition to the boiler feedwater is not sufficient to protect such remote areas from carbon dioxide induced corrosion, and often these lines are unprotected or require satellite feed of amines.

Amines having a relatively high volatility compared to the above treatment amines are known. For
 30 example, dimethylamine (DMA), trimethylamine (TMA), and diethylamine (DEA) have properties that make them desirable for use in corrosion inhibition in boiler/condensate systems. For example, DMA which has a DR of from 2 to 5, is an extremely strong base (pKa of 10.77) and due to its molecular weight is capable of neutralizing carbonic acid on an approximately 1:1 molar ratio. TMA is between 2 to 5 times more volatile than cyclohexylamine at boiler pressures from 689.5 to 10342.5 kPa (100 to 1500 psig). DEA has a
 35 distribution ratio (at 6985 kPa (1000 psig)) of 28. Cyclohexylamine is the most volatile neutralizing inhibitor commonly used in the treatment of steam boiler/condensate systems. Thus, it is believed that DMA, TMA, DEA and other low molecular weight amines would be more effective than cyclohexylamine and other amines used for condensate treatment in following and neutralizing carbon dioxide in the outlying areas of a condensate return system. However, the extreme volatility, i.e. flammability and high atmospheric vapour
 40 pressures, of low molecular weight amines has prevented the production of acceptable product formulations containing volatile, low molecular weight amines such as, for example, DEA, DMA and TMA for use in boiler/condensate system corrosion treatment.

The present invention provides a composition and method for controlling corrosion in boiler/condensate aqueous systems.

45 According to one embodiment of the present invention there is provided a method of controlling corrosion in boiler/condensate aqueous systems which comprises adding to the system an amount of at least one volatile, flammable, relatively low molecular weight amine by feeding to the system at least one, less volatile, relatively high molecular weight amine which when subjected to conditions of temperature and pressure in the system at least partially decomposes into the at least one relatively low molecular weight
 50 amine.

According to another embodiment of the present invention there is provided a method of controlling corrosion in a boiler/condensate aqueous system which comprises treating the system with an amount of a mixture of amines of varying relative molecular weights and volatilities by feeding to the system an amine having a relatively high molecular weight and relatively low volatility which when exposed to conditions of
 55 temperature and pressure in the system at least partially decomposes into low molecular weight, higher volatility amines.

The present invention also provides a corrosion control additive for boiler/condensate aqueous systems which comprises an amount of a mixture of amines of varying relative molecular weights, volatilities and

flammabilities, the mixture including at least one relatively high molecular weight amine and the relatively low molecular weight decomposition products thereof.

The method of the present invention comprises the addition of a relatively high molecular weight amine to the feedwater of a boiler/condensate water system. The high molecular weight amine partially decomposes at the conditions of temperature and pressure in the boiler/condensate steam system, either through hydrolytic cleavage or thermal degradation, to provide more volatile lower molecular weight amines. The lower molecular weight amines in combination with undecomposed high molecular weight amine provides corrosion control which is superior to the control from a blend of neutralizing amines from a single amine feed. Such a combination provides corrosion control by amines with a range of distribution ratios. The high molecular weight amine is selected so that at the typical temperatures and pressures of the boiler/condensate steam system, at least partial decomposition to lower molecular weight amines such as, for example, monobasic alkyl amines occur. Such lower molecular weight amines such as DMA, TMA and DEA are highly volatile and flammable so their addition to the system feedwater in that form presents problems in handling and shipping. Thus, the feed of a single, relatively high molecular weight amine which is relatively easy to handle gives rise in the boiler system to a mixture of several amines which cover a broad range of distribution ratios and thus provides effective coverage of even complex boiler/condensate systems.

The preferred relatively high molecular weight amine of the present invention is dimethylaminopropyl amine or N,N-dimethyl-1,3-propanediamine (DMAPA). DMAPA partially decomposes at common boiler conditions to provide monobasic amines such as, for example, dimethylamine (DMA) and trimethylamine (TMA). Methylamine and dimethylaminopropanol may also be produced. Other relatively high molecular weight amines may also be employed which will partially decompose at common boiler conditions. For example, dimethylaminoethanol (DEAE) will partially decompose at common boiler conditions to ethylaminoethanol (EAE) and diethylamine (DEA). The mechanism of decomposition is not clearly understood but it is believed to be a form of hydrolytic cleavage or thermal degradation.

The inventors of the present invention attempted to produce acceptable boiler water/condensate system control agent formulations containing a DMA and TMA and other volatile low molecular weight amines. Research into the effectiveness of TMA as a condensation system corrosion control agent indicated that TMA was 2 to 5 times more volatile than cyclohexylamine. Research also indicated that DMA has a DR of from 2 to 5, is an extremely strong base and is capable of neutralizing carbonic acid on approximately 1:1 molar basis. All of these properties indicated a possibility of improved condensate system control through the use of DMA or TMA. Attempts to develop product formulations containing low molecular weight amines which typically have extremely high atmospheric vapour pressures and are highly flammable were unsuccessful. These properties made the use of relatively low molecular weight amines such as, for example, DMA and TMA hazardous and complicated. In addition, DMA and TMA are hazardous to formulate and store, limiting their usefulness in commercial settings.

The inventors of the present invention discovered that a relatively high molecular weight amine could be formulated which when exposed to typical temperature and pressure conditions in a boiler system would partially decompose into the desirable, relatively volatile low molecular weight amines. By providing a relatively high molecular weight amine, only a single amine need be formulated, transported, stored and fed to a boiler system. The relatively high molecular weight of the feed amine results in a less volatile amine which is easier to transport, store and to feed. Proper formulation of the single relatively high molecular weight amine provides for partial decomposition at standard boiler temperature and pressure ranges. The relatively high molecular weight amine is formulated such that upon the partial decomposition relatively low molecular weight amines are formed. Thus, the single feed amine of the present invention provides for the in situ formation of a mixture of several amines in the boiler/condensate system. These several amines exhibit a broad range of distribution ratios to provide effective corrosion control even in complex boiler/condensate systems.

The preferred relatively high molecular weight amine of the present invention is dimethylaminopropylamine (DMAPA) or N,N-dimethyl-1,3-propanediamine. It has been found that the DMAPA is relatively easy to formulate, transport, store and feed as a single amine. When DMAPA is subjected to common boiler temperatures and pressures of from 689.5 to 10342.5 kPa (100 to 1500 psig), the DMAPA will partially decompose. The partial decomposition of DMAP forms DMA and TMA.

The properties of these components, including their DR is given in Table 1.

Table 1

Amine	Molecular Weight	Basicity (pKa)	Distribution Ratios			°C	Flash Pt. °F
			689.5 kPa (100 psig)	1379 kPa (200 psig)	4137 kPa (600 psig)		
DMAPA	102	10.0/8.2	1.1	1.9	2.0	29	84
DMA	45	10.8	2.4	2.1	3.3	16	60
TMA	59	9.8	15.3	12.6	28.0	-7	20

Whilst total decomposition of the high molecular weight amine may occur, it has been found that usually such decomposition is partial in nature.

The following lab scale experiment varified the formation of DMA and TMA.

A research scale, electrically heated test boiler was charged with nitrogen sparged (a mechanical deaeration), demineralized water. The water was supplied by high pressure pump to a D-configuration stainless steel boiler having an internal volume of approximately 5 litres. Two 4000 watt Incoloy 800 resistance heaters produced a steam rate of approximately 7.7 kg/hr. (17 lbs/hr.) at a steam pressure of 9997.8 kPa (1,450 psig) (correspond to a temperature of 312°C (593°F)). Cycles of concentration were held at approximately 15 by controlling boiler blowdown rate to 0.50 kg/hr. (1.1 lbs/hr.). The saturated steam produced was routed back into the feed tank and mixed with the original feedwater. This follows common industry practice where for economy the maximum amount of condensate is returned to the boiler as feedwater. The feedwater initially contained 200 ppm of DMAPA (Aldrich 99%) and 1.4 ppm hydrazine for deaeration. The feedwater (to which the condensed steam was recycled) was analysed by gas chromatography and DMA and TMA were quantitated by comparison to external standards. Table II summarises the results.

TABLE II

Sample	Elapsed Time (hrs.)	Feedwater Composition(ppm)			Conductivity (uS)
		DMA	TMA	pH	
12	22	5	9	10.35	160
13	46	11	16	10.40	195
14	79	20	25	10.65	200
15	94	25	32	10.35	230

As shown, the addition of the single amine, DMAPA resulted in a steadily increasing concentration of DMA and TMA with time. The elevation in pH is believed to be due to the formation of highly basic DMA while the increase in conductivity is believed to be due to the increasing concentrations of DMA and TMA in the steam, both of which are significantly more volatile than DMAPA. Testing at varying boiler pressures has indicated a relationship between boiler pressure and the rate at which DMAPA decomposes into DMA and TMA.

Additional testing with the relatively high molecular weight amine DMAPA has indicated that in addition to DMA and TMA, other relatively low molecular weight amines also form. The formation of methylamine (MA) and dimethylaminopropanol (DMAP) has been confirmed. The formation of other, relatively low molecular weight amines may also occur in the practice of the present invention.

Additional testing with the relatively high molecular weight amine diethylaminoethanol (DEAE) confirmed its partial decomposition into the volatile, relatively low molecular weight amines ethylaminoethanol (EAE) and diethylamine (DEA). This partial decomposition of DEAE occurred at conditions of temperature and pressure common to a typical boiler/condensate steam system.

As shown by the above data, the addition of a single select amine can give rise to the presence in a boiler/condensate system of a mixture of amines which provide a range of distribution ratios thereby

providing improved system wide corrosion control. Selection and formulation of a single, high molecular weight amine which will at least partially decompose to lower molecular weight amines which are more volatile allows the ease of a single amine feed to provide the efficiency of multiple amine treatment.

This efficiency is provided without the problems associated with the feeding of volatile, often highly flammable low molecular weight amines.

Claims

1. A method of controlling corrosion in boiler/condensate aqueous systems which comprises adding to the system an amount of at least one volatile, flammable, relatively low molecular weight amine by feeding to the system at least one, less volatile, relatively high molecular weight amine which when subjected to conditions of temperature and pressure in the system at least partially decomposes into the at least one relatively low molecular weight amine.
2. A method of controlling corrosion in a boiler/condensate aqueous system which comprises treating the system with an amount of a mixture of amines of varying relative molecular weights and volatilities by feeding to the system an amine having a relatively high molecular weight and relatively low volatility which when exposed to conditions of temperature and pressure in the system at least partially decomposes into low molecular weight, higher volatility amines.
3. A method according to claim 1 or 2, wherein the high molecular weight amine is dimethylaminopropylamine.
4. A method according to claim 3, wherein the low molecular weight amine includes dimethylamine and trimethylamine.
5. A method according to claim 1 or 2, wherein the high molecular weight amine is diethylaminoethanol.
6. A method according to claim 5, wherein the low molecular weight amine includes ethylaminoethanol and diethylamine.
7. A corrosion control additive for boiler/condensate aqueous systems which comprises an amount of a mixture of amines of varying relative molecular weights, volatilities and flammabilities, the mixture including at least one relatively high molecular weight amine and the relatively low molecular weight decomposition products thereof.
8. A corrosion control additive according to claim 7, wherein the mixture is formed by the in situ partial decomposition of the relatively high molecular weight amine.
9. A corrosion control additive according to claim 7 or 8, wherein the relatively high molecular weight amine is diethylaminoethanol.
10. A corrosion control additive according to claim 9, wherein the relatively low molecular weight decomposition products include ethylaminoethanol and diethylamine.
11. A corrosion control additive according to claim 7 or 8, wherein the relatively high molecular weight amine is dimethylaminopropylamine.
12. A corrosion control additive according to claim 11, wherein the relatively low molecular weight decomposition products include dimethylamine and trimethylamine.



DOCUMENTS CONSIDERED TO BE RELEVANT			EP 89306603.5
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. ⁴)
A	<u>US - A - 4 726 914</u> (FELLOWS et al.) * Totality * --	1-12	C 23 F 11/14
A	<u>US - A - 4 562 042</u> (MORAN) * Claims * --	1-12	
A	<u>US - A - 3 029 125</u> (HUMMEL) * Claims 1-3 * -----	1-12	
			TECHNICAL FIELDS SEARCHED (Int. Cl. ⁴)
			C 23 F C 02 F
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 19-09-1989	Examiner HAUSWIRTH
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			