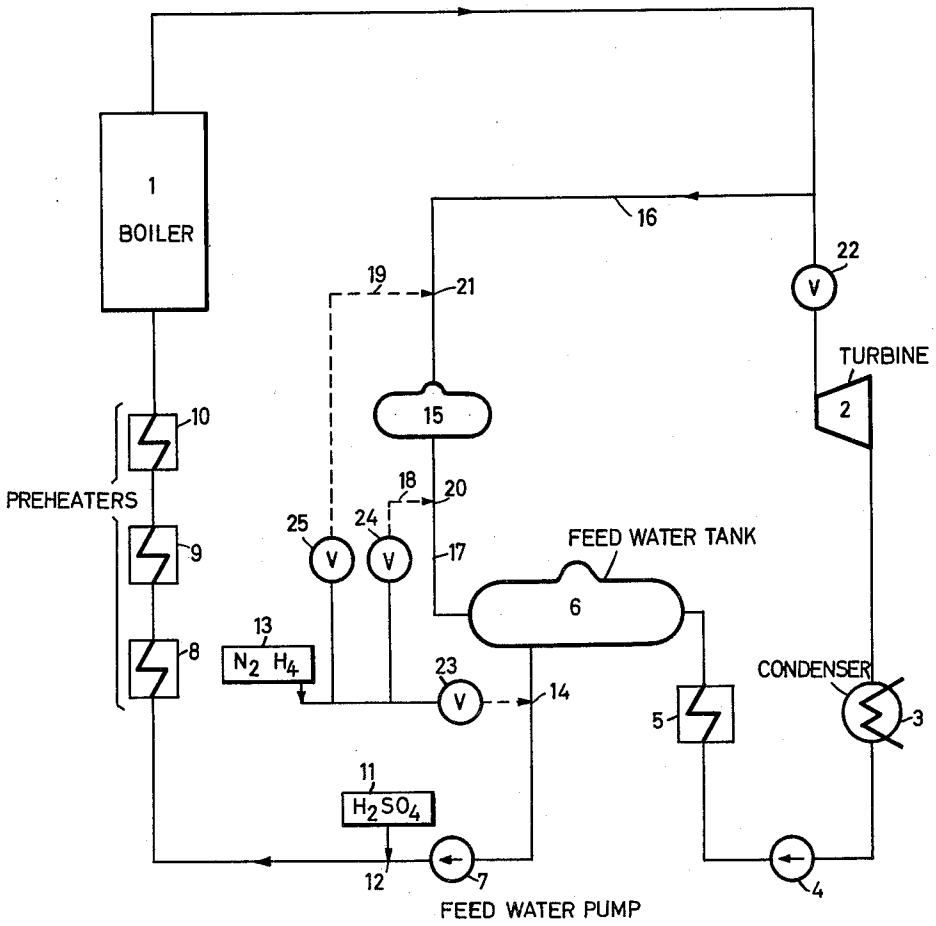
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METHOD OF REMOVING RUST FROM IRON-CONTAINING MATERIALS, PARTICULARLY FOR THE CLEANING OF BOILER PLANTS

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METHOD OF REMOVING RUST FROM IRON-CONTAINING MATERIALS, PARTICULARLY FOR THE CLEANING OF BOILER PLANTS

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Our invention relates to the cleaning and de-rusting of iron-containing materials, plants, or apparatus. It particularly, although not exclusively, relates to the cleaning of tube systems and boiler plant systems especially.

This application is a continuation in part of subsequently abandoned copending application Serial No. 726,386, filed April 4, 1958, by the same inventors.

Prior to starting operation, boiler, plants must be subjected to chemical cleaning or etching. For example, when erecting the plant the tube system may be subjected to rusting due to humid air, and it may also contain scale spots caused by welding and bending operations. Removal of such foreign matter is an indispensible requirement for satisfactory boiler and turbine operation.

The chemical cleanser utilized for this purpose, usually an acid solution employed together with an inhibitor, should be simple in chemical composition, and cheap, and should also possess an acid concentration such that the etched inner tube surfaces are attacked as little as possible. Moreover, the inhibitor should be independent of temperature in inhibitor function and in chemical stability, as far as possible.

The etching solutions heretofore used for such purposes in most cases consist of a 5 to 6% concentration of acid in conjunction with an inhibitor the sole purpose of which is to reduce the aggressiveness of the acid. The inhibitors in present use tend to lose their inhibiting properties at temperatures above 80° C. Furthermore the boiling-out of the tube systems with the known etching agents is very costly, because large quantities of acid, amounting to approximately one-third of the water content of the boiler tube system, must be circulated, and this must be done with acid-proof pumps equipped with correspondingly resistant inlet and outlet conduits. Unless all parts of the boiler tube system can be drained free of water, it is also difficult to neutralize the acid after completion of the etching operation. For reasons of safety, the tube systems of the latter type cannot be etched at all in the conventional manner, because it is extremely uncertain whether the undrained bodies of solution that may remain in particular portions of the tubes are fully neutralized. Sufficient protective layer (Fe_3O_4) is fully formed only after putting the boiler plant into normal operation; that is, when using conventional etching agents.

It is an object of our invention to avoid or minimize the above-mentioned difficulties. Another, more specific object of the invention, is to provide an improved method for de-rusting or cleaning which employs an etching solution having a considerably smaller acid concentration than prior etching solutions, the etching being satisfactorily performed with much smaller quantities of acid than heretofore found necessary.

To achieve these aims, and in accordance with a feature of our invention, we add to the said less concentrated etching acid one or more substances characterized by high temperature resistance and by the fact that the substance forms salts with the particular acid used only by addition compound formation. Said substance is termed "acid carrier."

In this manner the acid is bonded only temporarily in the form of an addition compound. This means that the acid is not lost with respect to the etching function. However, in order that the acid, initially so bound to the acid carrier, may be enabled to participate in the elimination of rust and in the formation of a protective coating, the etching solution together with the feed water are pre-heated to a temperature at which the compounded acid is liberated by thermal dissociation of the addition compound.

An acid carrier of particularly great efficacy, possessing the above-mentioned properties, is hydrazine. Moreover, it has an especial strong reduction effect upon the rust layers, and is also capable of forming a protective layer (Fe_3O_4) at the inner walls of the tubes. Furthermore it also reacts with the particular etching acid in the following manner:

At first the etching acid, for example hydrochloric acid, forms an addition compound. However, due to the said heating together with the feed water, the acid is again liberated and at first reacts with the rust and scale constituents to form iron chloride, whereas an OH-group is added to the hydrazine. The reaction of the iron chloride and the aqueous hydrazine solution produces iron hydroxide and regenerates free hydrochloric acid. The iron hydroxide represents the separated rust proper and is either drained from the boiler together with the feed water, or is separated from the feed water when a cyclic operation is involved. The more that the iron hydroxide is removed, the more the re-formation of acid is promoted.

Without limiting the invention thereby, we formulate the general types of reactions taking place and discussed above, as follows:

$$F_2O_3+N_2H_4\rightarrow Fe_3O_4+H_2O+N_2 \quad (1)$$

$$N_2H_4+HCl\rightarrow N_2H_4.HCl \text{ or } N_2H_4.2HCl \quad (2)$$

$$Fe_3O_4+HCl\rightarrow FeCl_2+FeCl_3+H_2O \quad (3)$$

$$FeCl_3+N_2H_2\rightarrow FeCl_2+HCl+N_2 \quad (4)$$

$$FeCl_2+H_2O\rightarrow Fe(OH)_2+HCl \quad (5)$$

The summary of the Reactions 1 to 5 is as follows:

$$F_2O_3 + N_2H_2 + H_2O \xrightarrow{HCl} Fe(OH)_2 + H_2 + N_2$$

Thus, as stated above, the free hydrochloric acid is regenerated.

Acting similarly to hydrazine are substances which form analogous salts with acid, for example the inorganic and organic nitrogen containing bases, such as ammonia, hydroxylamine, and organic amines. However, hydrazine is more advantageous.

The heating of the boiler can be effected in various ways. The etching or boiling-out is effected either successively with the individual components of the solution, or simultaneously with the complete solution. In the first case, the pre-heated feed water is first provided with hydrazine with the aid of a dosage pump, and the solution is then permitted to act, depending upon the particular conditions, for a prolonged length of time, for example a full day. The most favorable effect is obtained by circulating the feed water. In this case, although the scale layers are not dissolved, the rust coatings go into solution and the desired formation of a protective coating commences, simultaneously. After such pre-treatment, the etching acid, for example hydrochloric acid, is fed into the boiler the next following day, preferably maintaining the correct pH and temperature. The acid then reacts together with the hydrazine as described above and also dissolves the residual scale layers.

When the boiling-out is effected with the complete etching solution, mentioned above as the second way of procedure, it is preferable to at first introduce hydrazine into the pre-heated feed water, while the feed water is

kept in circulation. Subsequently, the proper or predetermined dosage of hydrochloric acid is added. In each case hydrazine is preferably fed into the boiler until a maximum pH-value of 9 is obtained. The pH-value is then lowered to about 3.5 by adding the hydrochloric acid to the feed water. The etching acid solution thus is given an acid concentration of 0.001%. This corresponds to 0.3 ml. of 36% acid solution per liter of fully de-salted diluting water.

The attack on the bare surface of a non-alloyed carbon steel, at 80° C. and a pH-value of about 3.5 amounts to approximately 2 grams per square meter per hour. This is barely twice the value of attack at 20° C. The consumption of hydrazine for one gram of rust (Fe_2O_3) amounts to only 33 milligrams. Due to the efficacy of the very low acid concentration, the quantities of acid utilized in the process are much smaller than usual. Consequently, with the etching solution according to the invention it is also possible to etch boilers whose tube system cannot be fully drained of water. The neutralization of the acid solution after etching can readily be effected by increasing the pH-value to 7, that is, by renewed supply of hydrazine solution.

If the available feed water is insufficient for draining the dissolved rust together with the eaching liquid, that is, if the etching is performed in the circulatory method, then it is preferable, for separating the rust (iron hydroxide) to insert an intermediate vessel into the circulation system, in which vessel the iron hydroxide can precipitate. If the feed water tank of the plant already possesses built-in structure that permits the dissolved rust to be deposited thereon, the feed water tank can be used for the purpose of rust separation, in lieu of using a separate vessel. The circulatory method has the advantage of saving chemicals, and also of avoiding loss of the heat that was used to heat the feed water.

Instead of using separate acid pumps when cleaning the boiler plant with the etching solution according to the invention, the normal feed water pump of the plant may be used for circulating the etching agent and the feed water. For this purpose the acid is supplied into the system downstream of the feed water pump, that is, ahead of the water entrance point of the boiler, and the hydrazine solution is injected at a system point ahead of the intermediate container, that is still ahead of the feed water pump. In this manner it is made certain that the feed water etching agent mixture delivered by the feed water pump is neutral so that the pump is not damaged. As a further result, the previously necessary acid-proof entrance and exit lines are also eliminated. By virtue of the fact that the hydrazine injection point is located still ahead of the intermediate container there results the further advantage that the iron hydroxide is precipitated in the intermediate container with particularly great intensity.

Subsequent to the etching treatment, removal of silica deposits in the boiler can also be effected. Such removal of silica is known as such for turbines, and may also be performed with steam boilers with the aid of a 0.04% caustic soda solution (sodium hydroxide solution) at temperatures between 100 and 200° C. The spent caustic solution is replenished by means of a dosage pump. After the silicic acid, which has gained access to the interior of the boiler (in the manufacturing process and during the assembly and installing work) has gone into solution, the caustic solution is substituted by pure water, thus thoroughly washing the boiler. If desired, hydrazine can be added to the water.

The cleaning method disclosed herein is not limited in utility to the etching of boiler plants. It may also be used for the etching of other metallic tube systems, as well as of metal bodies in general.

When, in addition to removing rust and scale, it is also desired to remove silicic acid or silica deposits, the two can be combined into a single operation, to a substantial extent. If, subsequently to the acid treatment, the removal of silica is effected by means of caustic soda solution, the latter solution effects only a slight dissolution of silicic acid at temperatures up to 100° C. Furthermore, relatively large quantities of washing water are required to completely remove the caustic solution from the boiler. According to a further feature of the invention, it is feasible to satisfactorily combine the rust and scale removal with the removal of silicic acid, to obtain both results by a single operation. This can be effected by applying an etching solution of the above-described type. Such a solution used for simultaneous removal of silicic acid contains a mixture of hydrochloric acid or sulfuric acid on the one hand and hydrofluoric acid or ammonium fluoride or ammonium bifluoride on the other hand. The mixing ratio of hydrochloric or sulfuric acid to hydrofluoric acid may be approximately 3:1. When using ammonium fluorides, the mixing ratio is preferably 4:1 approximately. The temperature of the feed water in these cases is preferably at least 100° C. The etching solution can be applied in a manner similar to that already described above. That is, the pH-value of the feed water is at first adjusted to a given value, preferably about 9, with the aid of hydrazine preferably, or other amino compounds. During the circulatory pumping of this feed water through the entire tube system to be de-rusted, a mixture of hydrochloric acid, or sulfuric acid, with hydrofluoric acid or ammonium fluoride or ammonium bifluoride, is added to the fed water prior to its entrance into the boiler, the addition being rated for adjusting to a pH-value of approximately 3 to 4.

By means of the addition of the hydrofluoric acid, or of ammonium fluoride, from which latter the fluoric acid is liberated by the hydrochloric or sulfuric acid, the silicic acid is placed into solution, which function is aside from the removal of rust and scale. The silicic acid is thereafter removed by the subsequent washing with water. The advantages of this method are that the cleaning of the boiler in respect to silicic acid residues is more complete than the previously employed method in which caustic soda solution is used, and the losses of feed water are reduced. Moreover, the time required for the chemical cleaning is reduced to a substantial and significant extent.

The schematic flow diagram indicates one embodiment of the invention. Since the invention involves processes which must generally be carried out with a completed, already installed, and perhaps previously operated boiler plant, the specific requirements vary because boiler plants may depart from each other in the construction, and in the arrangement, of individual components. In the enclosed sketch we have assumed the use of a steam power plant in which a boiler **1** supplies steam to a turbine **2**. The turbine condenser is at **3**, the condensate pump at **4**, the low-pressure feed water pre-heater at **5**, and the feed water tank, with de-gassing equipment at **6**. The working medium is conveyed from feed water tank **6** to the boiler by means of the feed water pump **7**; in practice there are several parallel connected pumps. Three steam-heated, steam-pressure, pre-heaters **8**, **9** and **10** may be provided. The steam supply leads of the regenerative pre-heaters are omitted for simplicity of illustration. Also omitted are all further components of the plant which are not required for the understanding of the invention.

The acid, for example sulfuric or hydrochloric, is injected at a location behind the feed water pump; the acid, available in a tank **11**, being introduced into the circulation system at injection point **12**.

The hydrazine from tank **13** is introduced at a suitable location head of the feed water pump **7**. In a simple case, this injection point, indicated by numeral **14**, may be located at the exit of the feed water tank **6**. The additional intermediate vessel **15** is mentioned above. The intermediate container **15** may serve various purposes, for example to provide for an intermediate reduction in pres-

sure. A suitable starting line **16** extends from the boiler exit to the container **15** which, in turn, is connected through a line **17** with the feed water tank **6**. It will be understood that the feed water tank **6** itself may serve as an intermediate container, so that the rust may precipitate in that tank. In order to indicate all modes of operation, the broken-line connections **18** and **19** are shown connected to the injection points **20** and **21**, so that the acid carrier can be supplied selectively to the various locations.

Prior to the boiling-out or etching operation, a stop valve **22** closes the line leading to the turbine **2**. Depending upon which particular inhibitor location is to be used, the various stop valves **23**, **24** and **25** can be opened or closed.

The above disclosure is identical with that found in our prior application, Serial No. 726,386.

In the copending application we thus disclosed a method for de-rusting of iron-containing materials and plants or apparatus, which is particularly useful for the cleaning of the tube systems and boiler plants, and in which is employed an etching solution having an addition, consisting of substances of high temperature resistance which form salts with the etching solution only by addition compound formation. The resulting effect is not an inhibitor action, as such. The additional chemicals employed serve as carriers of the etching acid, due to the fact that they either react with the acid under thermal action to form salts which can be readily disassociated into their component substances, or which salts inherently react acidically. Suitable as such substances are, for example, ammonia, hydroxylamine or organic amines, as stated above. As indicated above, this method can further be improved by obtaining simultaneously removal of silica. For this purpose, an etching solution is used which contains a mixture of hydrochloric acid or sulphuric acid on the one hand, and fluoric acid or ammonium fluoride or ammonium bifluoride, on the other hand. We explain again that this embodiment of the method is performed by heating the feed water of the boiler plant to approximately at least 100° C., then treating the heated feed water with a solution of hydrazine or other amino compounds to reduce the pH value of the feed water down to approximately 9, and thereafter depressing the pH value down to about 3 to 4 by addition of the above-mentioned fluoride-containing mixture.

In the cleaning methods described above it is sometimes a disadvantage that the entire rust and tinder occurs as a fine sludge. Special expedients are necessary to remove this sludge. For example, the sludge must be washed out of the boiler by using water having a high flow velocity. Even then, there may remain the danger that nests of sludge will form in those parts of the boiler where the flow remains relatively weak as is the case particularly in the collector portions of the boiler plant. The sludge may also result in trouble during the subsequent operation of the boiler plant.

It is a particular purpose of our invention to completely eliminate the sludge formation without departing from the cleaning principle described in the above-mentioned pending application, and without foregoing its advantages. Accordingly, we add to the etching solution substances which form internal complex compounds with the dissolved iron. Suitable as such substances, for example, are hydroxyl-group containing organic substances, viz. carbohydrates and hydroxyaliphatic acids. These are, for example, vinous acid (tartaric acid), grape sugar, cane sugar and the like. However, citric acid is preferred. The pre-treatment of the plants to be cleaned, can be carried out in the same manner as is described above and in application Serial No. 726,386. After the removal of oil with the aid of oil dissolving means the pH is increased. The increase of the pH up to the value 9 is preferably effected with the aid of hydrazine or other amino compounds which form salts with acids. Subsequently, as already mentioned above, the lowering of the pH value to about 3 to 4 can be effected with the aid of acids.

Prior to adding acid, the water to be circulated through the plant, by pumping, is provided, according to an embodiment of the invention, with mixed substances which enter into internal complex compounds with the dissolved iron. When the salts of these complex-forming acids or undissociated complex-forming salts are used, then a simultaneous addition is made of hydrochloric acid or sulphuric acid, if desired, in conjunction with fluoric acid or fluorides for the purpose of eliminating silica. In practice, all possible combinations with the chemicals mentioned above and in prior application Serial No. 726,386, or mentioned in the fourth paragraph above, are applicable. For most advantageous results it is essential that the quantity of the substances, capable of forming complex compounds with iron, be sufficient to exclude the formation of sludge within the boiler or other plants to be cleaned. Therefore the quantity of complex-forming substances added depends upon the amount of rust to be dissolved. The cleaning process is preferably performed for a period of about 24 to 48 hours, at temperatures between 100 and 150° C.

It is within the purview of the invention to substitute or to employ other hydroxy organic compounds which are known to enter with iron or rust into internal complex compounds, or which can be determined by test to have this property. Water-soluble poly-, or dissimilar poly-functional hydroxy organic compounds of non-basic character and consisting of oxygen, hydrogen, and carbon are preferred, that is, those having a second substituent different from the hydroxy group and of non-basic character and which form water-soluble or dispersible complex compounds with iron or iron oxide.

We claim:

1. In a process of de-rusting the surface of an iron-containing material in which a hot acidic aqueous etching solution is contacted with said surface, the acid being taken from the group consisting of hydrochloric and sulfuric acid, the improvement comprising carrying out said process in the presence of a substance which can form a salt with the acid by addition compound formation, the salt being dissociated in the hot solution, the process being carried out at a temperature above about 90° C. at an acid pH of not below about 3, the acid being in a concentration of less than a hundredth of a percent, said substance being taken from the group consisting of inorganic and organic nitrogen containing basic substances, the concentration of said substance being not greater than that which would give a pH of about 9 in water alone.

2. In a process of de-rusting the surface of an iron-containing material in which an acidic aqueous etching solution is contacted with said surface, the improvement comprising carrying out said process in the presence of a substance which can form a salt with the acid by addition compound formation, the salt being dissociated in the solution, the process being carried out at a temperature above 90° C. at an acid pH of not below about 3, the acid being in a concentration of less than a hundredth of a percent, said substance being taken from the group consisting of ammonia, hydroxylamine, hydrazines, and organic amines, the concentration of said substance being not greater than that which would give a pH of about 9 in water alone, the acid of the etching solution being at least one substance taken from the group consisting of hydrochloric and sulfuric acid.

3. In a process of de-rusting the surface of an iron-containing material in which aqueous hydrochloric acid etching solution is contacted with said surface at above 90° C., the improvement comprising carrying out said process in the presence of hydrazine, the etching acid having a concentration of .004 to .0004%, the hydrazine

being employed in an amount not greater than about that which will combine to form a salt with said acid.

4. In a process of de-rusting the surface of an iron-containing material in which an aqueous sulfuric acid etching solution is contacted with said surface at above 90° C., the improvement comprising carrying out said process in the presence of hydrazine, the etching acid having a concentration of .004 to .0004%, the hydrazine being employed in an amount not greater than about that which will combine to form a salt with said acid.

5. In a process of de-rusting the surface of an iron-containing material in which an aqueous acidic etching solution is contacted with said surface, the acid being taken from the group consisting of hydrochloric and sulfuric acid, the improvement comprising carrying out said process in the presence of hydroxylamine, the acid being in a concentration of not more than about .004%, the hydroxylamine being employed in an amount not greater than that which will form a salt with said acid.

6. In a process of removing rust and silica deposits in steam boilers, in which a hot aqueous hydrochloric acid etching solution is circulated through the boiler at at least 90° C., the improvement comprising adding thereto hydrazine and a compound of the group consisting of hydrofluoric acid and fluorides of ammonia, the hydrazine being employed in an amount such that the circulating solution passed through the boiler is acidic, the hydrochloric acid being in a concentration of not more than a hundredth of a percent, the hydrazine being employed in an amount not greater that that which will combine with said hydrochloric acid to form a salt.

7. In a process of removing rust and silica deposits in steam boilers, in which an aqueous sulfuric acid etching solution is circulated through the boiler at at least 90° C., the improvement comprising adding thereto hydrazine and a compound of the group consisting of hydrofluoric acid and fluorides of ammonia, the concentration of the hydrazine being not greater than that which would give a pH of about 9 in water alone, the hydrazine being employed in an amount such that the circulating solution passed through the boiler is acidic, the sulfuric acid being in a concentration of not more than a hundredth of a percent.

8. In a process of removing rust and silica deposits in steam boilers, in which an acidic aqueous etching solution is circulated through the boiler, the acid being taken from the group consisting of hydrochloric and sulfuric acid, the improvement comprising adding thereto hydrazine and a compound of the group consisting of hydrofluoric acid and fluorides of ammonia, the concentration of the hydrazine being not greater than that which would give a pH of about 9 in water alone, the hydrazine being employed in an amount such that the circulating solution passed through the boiler is acidic, the etching solution circulating in the boiler being at a temperature of at least 100° C. and the pH of the etching solution being in the range of about 3 to 4.

9. In a process of de-rusting the internal iron-containing surfaces of boilers, in which an acidic aqueous etching solution is circulated in contact with said surfaces, the improvement comprising carrying out said process in the presence of hydrazine, the acid being hydrochloric acid, the pH of the circulated solution being in the range of about 3.0 to 4.0, corresponding to an acid concentration of about 0.004 to 0.0004%.

10. In a process of de-rusting the internal iron-containing surfaces of boilers, in which an acidic aqueous etching solution is circulated in contact with said surfaces, the improvement comprising carrying out said process in the presence of hydrazine, the acid being sulfuric acid, the pH of the circulated solution being in the range of about 3.0 to 4.0, corresponding to an acid concentration of about 0.004 to 0.0004%.

11. In a process of de-rusting the internal iron-containing surfaces of steam boilers, in which a circulating hot etching solution comprising acidified boiler feed water is pumped through the boiler, the acid of the acidified feed water being taken from the group consisting of hydrochloric and sulfuric acid, the improvement comprising adding hydrazine to the feed water in an amount at least sufficient to make it alkaline, the hydrazine being added in the feed water flow path in advance of the pump, and adding the etching acid to the feed water after it leaves the pump, whereby the pump is not subjected to attack by acid solution, the pH of the circulated solution being in the range of about 3.0 to 4.0, corresponding to an acid concentration of about 0.004 to 0.0004%.

12. In a process of de-rusting the internal iron-containing surfaces of steam boilers, in which a circulating hot etching solution comprising acidified boiler feed water is pumped through the boiler, the improvement comprising adding hydrazine to the feed water in an amount at least sufficient to make it alkaline, the hydrazine being added in the feed water flow path in advance of the pump, and adding the etching acid to the feed water after it leaves the pump, whereby the pump is not subjected to attack by acid solution, said acid being hydrochloric acid, the pH of the circulated solution being in the range of about 3.0 to 4.0, corresponding to an acid concentration of about 0.004 to 0.0004%.

13. In a process of de-rusting the internal iron-containing surfaces of steam boilers, in which a circulating hot etching solution comprising acidified boiler feed water is pumped through the boiler, the improvement comprising adding hydrazine to the feed water in an amount at least sufficient to make it alkaline, the hydrazine being added in the feed water flow path in advance of the pump, and adding the etching acid to the feed water after it leaves the pump, whereby the pump is not subjected to attack by acid solution, said acid being sulfuric acid, the pH of the circulated solution being in the range of about 3.0 to 4.0, corresponding to an acid concentration of about 0.004 to 0.0004%.

14. In a process of de-rusting the internal iron-containing surfaces of steam boilers, in which an etching solution comprising acidified hot boiler feed water is pumped through the boiler, the improvement comprising adding hydrazine to the feed water, in its circulating flow path in advance of the pump, to adjust to a pH of the range of about 8 to 9, adding hydrochloric acid to the feed water after it leaves the pump, said acid being added to produce an etching solution having a pH in the range of about 3.0 to 4.0, and passing the latter solution to the boiler, the etching acid having a concentration of not more than a hundredth of a percent.

15. In a process of removing rust and silica deposits in steam boilers, in which an acidic aqueous etching solution is circulated through the boiler, the acid being taken from the group consisting of hydrochloric and sulfuric acid, the improvement comprising adding thereto hydrazine and a compound of the group consisting of hydrofluoric acid and fluorides of ammonia, the hydrazine being employed in an amount such that the circulating solution passed through the boiler is acidic, the concentration of the hydrazine being not greater than that which would give a pH of about 9 in water alone, the circulation being carried out by a feed water pump, the hydrazine being added to the feed water in advance of the pump in an amount at least sufficient to neutralize the feed water, to obviate acid attack on the pump, the etching acid and the said compound being added after the feed water leaves the pump, the circulated etching solution having an acid concentration of not more than 0.004%.

16. In a process of removing rust and silica deposits in steam boilers, in which an acidic aqueous etching solution is circulated through the boiler, the improvement comprising adding thereto hydrazine and a compound of the group consisting of hydrofluoric acid and fluorides of ammonia, the feed water being heated to at least about 100° C., the hydrazine being added to the circulation of

feed water to adjust it to a pH of about 9, subsequently adding an etching acid of the group consisting of hydrochloric and sulfuric acids, and also subsequently adding said compound, the circulated etching solution having an acid concentration of not more than about 0.004%.

17. In a process of de-rusting the internal iron-containing surfaces of boilers, in which an acidic aqueous etching solution is circulated in contact with said surfaces, the acid being taken from the group consisting of hydrochloric and sulfuric acid, the improvement comprising carrying out said process in the presence of hydrazine, the hydrazine being added first and the solution recirculated to cause the rust coatings in the boiler to go into solution and to commence the formation of a protective iron oxide coating, the etching acid being added later, the circulated etching solution having an acid concentration of less than one hundredth of one percent.

18. In a process of de-rusting the surface of an iron-containing material in which an acidic aqueous etching solution is contacted with said surface, the acid being taken from the group consisting of hydrochloric and sulfuric acid, the improvement comprising carrying out said process in the presence of hydrazine, the process being carried out at a temperature above 90° C. at an acid pH of not below about 3, the etching acid being in a concentration of not more than about 0.004%, the improvement further comprising including in the etching solution an hydroxy organic compound which forms an internal complex compound with dissolved iron in amount sufficient to substantially eliminate sludge formation.

19. In a process of de-rusting the surface of an iron-containing material in which an acidic aqueous etching solution is contacted with said surface, the acid being taken from the group consisting of hydrochloric and sulfuric acid, the improvement comprising carrying out said process in the presence of a substance which can form a salt with the acid by addition compound formation, the salt being dissociated in the solution, the process being carried out at a pH of about 3 to 4, at a temperature above 90° C., the circulated etching solution having an acid concentration of less than one hundredth of one percent, said substance being taken from the group consisting of inorganic and organic nitrogen containing basic substances, the improvement further comprising including in the etching solution an hydroxy organic compound which forms an internal complex compound with dissolved iron in amount sufficient to substantially eliminate sludge formation.

20. In a process of de-rusting the surface of an iron-containing material in which an acidic aqueous etching solution is contacted with said surface, the acid being taken from the group consisting of hydrochloric and sulfuric acid, the improvement comprising carrying out said process in the presence of a substance which can form a salt with the acid by addition compound formation, the salt being dissociated in the solution, the process being carried out at a temperature above 90° C., the circulated etching solution having an acid concentration of less than one hundredth of one percent, said substance being taken from the group consisting of ammonia, hydroxylamines, hydrazines, and organic amines, the improvement further comprising including in the etching solution an hydroxy organic compound which forms an internal complex compound with dissolved iron in amount sufficient to substantially eliminate sludge formation.

21. In a process of de-rusting the surface of an iron-containing material in which a dilute acidic aqueous etching solution is contacted with said surface, the improvement comprising carrying out said process in the presence of a substance which can form a salt with the acid by addition compound formation, the salt being dissociated in the solution, the process being carried out at a temperature above 90° C. at a pH between 3 and 4, said substance being taken from the group consisting of ammonia, hydroxylamines, hydrazines, and organic amines, the acid of the etching solution being at least one substance taken from the group consisting of hydrochloric and sulfuric acid at a concentration of said acid of less than a hundredth of one percent, the improvement further comprising including in the etching solution a water-soluble hydroxy organic compound which forms an internal complex compound with dissolved iron, in amount sufficient to substantially eliminate sludge formation.

22. The proces of claim 21 in which the said substance is hydrazine and the hydroxy organic compound is taken from the group consisting of tartaric acid, citric acid, and sugars.

23. The process of claim 21 in which the said substance is hydrazine and the hydroxy organic compound is taken from the group consisting of hydroxyaliphatic acids and carbohydrates.

24. In a process of de-rusting the internal iron-containing surfaces of steam boilers, in which an etching solution comprising acidified hot boiler feed water is pumped through the boiler, the improvement comprising adding hydrazine to the feed water, in its circulating flow path in advance of the pump, to adjust to a pH of the range of about 8 to 9, adding hydrochloric acid to the feed water after it leaves the pump, said acid being added to produce an etching solution having a pH in the range of about 3.0 to 4.0, the hydrochloric acid concentration of the etching solution being less than one hundredth of one percent and passing the latter solution to the boiler, the etching solution pumped through the boiler including therein an hydroxy organic compound which forms an internal complex compound with dissolved iron, said hydroxy compound being selected from the class of water-soluble poly-functional organic compounds consisting of oxygen, hydrogen and carbon.

25. In a process of de-rusting the surface of an iron-containing material in which a dilute acidic aqueous etching solution is contacted with said surface, the improvement comprising carrying out said process in the presence of a substance which can form a salt with the acid by addition compound formation, the salt being dissociated in the solution, said substance being taken from the group consisting of ammonia, hydroxylamines, hydrazines, and organic amines, the acid of the etching solution being at least one substance taken from the group consisting of hydrochloric and sulfuric acid at a concentration of less than one hundredth of one percent, the feed water being at first at least about 100° C., said substance being incorporated therewith, the pH of the feed water being thereby adjusted to approximately 9, adding a water-soluble organic hydroxy compound which forms a complex compound with dissolved iron, a sufficient amount of the compound being added to dissolve the rust, and thereafter adding additional etching acid to the etching solution to depress the pH to the range of about 3 to 4.

26. The process of claim 25, the substance being hydrazine, the acid being hydrochloric acid, the organic hydroxy compound being citric acid.

27. The process of claim 25, the substance being hydrazine, the acid being hydrochloric acid, the hydroxy organic compound being taken from the group consisting of water-soluble hydroxyaliphatic acids and carbohydrates.

28. In a process of removing rust and silica deposits in steam boilers, in which an acidic aqueous etching solution is circulated through the boiler, the acid being taken from the group consisting of hydrochloric and sulfuric acid, the improvement comprising adding thereto hydroxylamine and a compound of the group consisting of hydrofluoric acid and fluorides of ammonia, the hydrazine being employed in an amount such that the circulating solution passed through the boiler is acidic, the circulation being carried out by a feed water pump, the hydroxylamine being added to the feed water in advance of the pump in an amount at least sufficient to neutralize

the feed water, to obviate acid attack on the pump, the etching acid and the said compound being added after the feed water leaves the pump, the improvement further comprising including in the etching solution an hydroxy organic compound which forms an internal complex compound with dissolved iron in amount sufficient to substantially eliminate sludge formation, the circulated etching solution having a pH of not below about 3, the etching acid being in a concentration of less than a hundredth of a percent.

29. In a process of removing rust and silica deposits in steam boilers, in which an acidic aqueous etching solution is circulated through the boiler, the circulated etching solution being taken from the group consisting of hydrochloric and sulfuric acid and being in a concentration of less than a hundredth of a percent, the improvement comprising adding thereto hydrazine and a compound of the group consisting of hydrofluoric acid and fluorides of ammonia, the feed water being heated to at least about 100° C., the hydrazine being added to the circulation of feed water to adjust it to a pH of about 9, subsequently adding an etching acid of the group consisting of hydrochloric and sulfuric acids, and also subsequently adding said compound, the improvement further comprising including in the etching solution an hydroxy organic compound which forms an internal complex compound with dissolved iron in amount sufficient to substantially eliminate sludge formation, the circulated etching solution having an acid pH of not below about 3.

30. The process of claim 2, the said substance being hydroxylamine.

31. A process of de-rusting the surface of iron-containing material, comprising contacting said surface with an aqueous etching solution heated to above 90° C., said solution containing hydrazine and an acid taken from the group consisting of hydrochloric and sulfuric acid, the acid being in a concentration of less than one hundredth of a percent, the hydrazine content being not greater than that which would give a pH of about 9 in water alone, the acid lowering said pH to an acid pH not below about pH 3.5, the hydrazine serving to temporarily form a salt with the acid, said acid being released by dissociation of the salt upon heating the solution.

32. The process defined in claim 31, the acid being hydrochloric acid.

33. The process of claim 2, the etching solution also containing citric acid to form a complex compound with the dissolved iron.

34. The process of claim 24, the hydroxy compound being citric acid.

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