

1

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REMOVAL AND INHIBITION OF SCALE FORMATION IN STEAM GENERATION

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This invention is concerned with reduction and removal of scale in steam boilers. More specifically, the present invention is concerned with the prevention and removal of scale in evaporators, feedwater heaters, economizers, boilers and other parts of steam generating systems.

A troublesome problem encountered in steam boilers where water is boiled at superatmospheric pressures to generate steam is the tendency of such water containing any hardness constituents to deposit this hardness on the heat exchanging surfaces in the form of scale. Such scale deposition tends to reduce the heat transfer across the heat exchanging surface with resultant increased tendency of the metal to overheat. A most serious aspect of such a problem is one of rupture of boiler heat exchange surfaces due to the aforementioned scale deposition.

A number of prior art materials have been suggested to remove and particularly to inhibit boiler scale. Such materials as tannins, modified lignins, alginates and other organic substances of relatively complex molecular configuration have been employed. These materials while useful have one or more deficiencies. For example, their employment may result in boiler oxidation, metal surface decomposition and undesirable coloring which may result in steam contamination by carryover. In some instances known boiler additives require relatively large amounts to effectively inhibit scale. In other situations only certain scale types are affected by conventional types of organic boiler additives. It would therefore be of advantage to the art to provide a treatment of boiler scale which will avoid many of the just-mentioned disadvantages, and particularly be effective at relatively low dosage levels. Moreover, of such a boiler treatment could be developed whereby a wide variety of scale types were inhibited and/or removed upon application, such boiler process would become readily acceptable among those concerned.

It therefore becomes an object of the invention to provide a novel process of both removing and inhibiting scale formation in boilers.

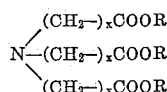
Another object of the invention is to provide a new class of boiler scale preventing compositions which are useful for treatment of a wide variety of different scale-inducing materials.

Other objects will appear hereinafter.

In accordance with the invention it has now been found that salts of nitrilotricarboxylic acids are effective in removing and inhibiting scale formation in boilers under conditions in which steam is generated under pressures ranging from about 15 p.s.i. to about 1100 p.s.i. In the broadest aspects of the invention sufficient salt is added to the boiler water to accomplish the removal and inhibition of undesirable scale.

The type of nitrilotricarboxylic acid salts useful in the invention fall within the following general structural formula:

2



where x is an integer of from 1 to 2, and R is a radical selected from the group consisting of hydrogen and an alkali metal, with at least one occurrence of R being an alkali metal radical.

In the practice of the invention the salts of nitrilotricarboxylic acid, preferably nitrilotriacetic acid salts and most preferably the trisodium salt of nitrilotriacetic acid may be added either to the boiler feedwater or directly to the water in the boiler where the steam is generated. It is greatly preferred that the boiler water from which the steam is generated has a pH within the range of 9 to 12 and more preferably 9 to 11. It has been determined that the dosage range to accomplish the objects of the invention should preferably be at least 0.1 p.p.m. and most preferably 0.1-1000 p.p.m.

The boiler additives of the invention may be added in solution form or in solid form such as in the shape of briquettes which may also contain soda ash, phosphates or other materials to be added to the water for specific purposes. In the most preferred practice to accomplish close additive control, the salts are added in aqueous solution form wherein the active ingredient comprises from about 10% up to the maximum of solubility of the salt in water.

In some instances an alkali material such as, for example, caustic soda, sodium carbonate or an alkaline phosphate may be required to adjust the boiler water to within the desired pH range.

As mentioned above a particularly preferred species of boiler additive due to low cost, excellent activity and availability is the trisodium metal salt of nitrilotriacetic acid. However, it should be understood that any alkali metal such as lithium and potassium may be used to form the cation constituent of the salt additives.

The boiler treating agents of the invention may be used to inhibit any scale forming material such as calcium and magnesium phosphates, carbonates, silicates, etc. In addition, use of the salt compositions of the invention also prevents build-up of deposits of magnetic iron oxides upon the heat exchange surfaces of the boilers.

Again, while the boiler additives described herein are particularly useful in inhibiting or preventing scale in steam boilers, they are likewise useful in removing already formed scale adhering to the metal surfaces of the boiler equipment.

It was the more surprising and unexpected that the above described salts were active in performing boiler scale inhibition and removal roles in view of prior literature. For example, U.S. Patent 2,396,938 states that at least four $-\text{CH}_2\text{COOM}$ groups (where M is an alkali metal) must be present for satisfactory results in boilers. We have now discovered that such requirement is not necessary, at least within the pressures wherein the salts of the invention are operable. In point of fact, as will be seen hereinafter, in some instances, the nitrilotriacetic acid salts and particularly the trisodium salt (NTA Na_3) are superior to such materials containing four carboxyl groups as ethylenediaminetetraacetic acid, tetrasodium salt, (EDTA Na_4).

EVALUATION OF THE INVENTION

The test equipment used in the following test runs consists of a No. 2 inclined tube experimental boiler with

natural thermal circulation. Volume at normal operating level was 0.56 gallon. The water level itself was automatically controlled by 3 insulated electrodes which made contact with the boiler water to operate relays which controlled the feedwater pump and heating element. Pressure control was by manual adjustment of a needle valve in the condensed steam line. Boiler test specimens were low carbon steel tubes, 1½" O.D. x 10" long, closed at one end and flanged at the other. The tubes were bolted in the boiler at an angle of 30° from the horizontal with the closed end down. Heat was applied to the inside and water surrounded the outside. A soft corrugated copper gasket was used to seal the tube in the boiler. The test surface itself was cleaned and polished with No. 3/0 emery paper before each test. Tests were run in absence of chemical (blank) and in a comparative manner with varying dosages of test chemical. Percent scale prevention was then calculated by measuring deposition of scale upon the test specimen with benefit of chemical boiler additive, while using the blank run as a basis of comparison and a base of 0% reduction.

The water used as test medium was 1 part Chicago tap water diluted with 8 parts zeolite softened Chicago tap and 11 parts distilled water to give a feedwater having a 5 p.p.m. calcium and 2 p.p.m. magnesium hardness. This feedwater also contained sufficient natural alkalinity to give a hydroxyl alkalinity residual of 300–350 in the boiler water (pH 10–11). Lastly, soluble phosphate salt was added in an amount sufficient to give a 3 p.p.m. PO₄ level. The above described test water was used unless otherwise stated.

Example I

In the first series of tests the effect of pressure upon performance of NTA Na₃ was investigated. Results are as follows:

TABLE I

P.p.m.	Pressure, p.s.i.	Percent Scale Prevention
18	250	95
27	250	90
18	800	70
36	800	75
36	1,200	45
36	1,500	0
36	800	0

Thus it can be seen that within a pressure range of relatively low pressure up to about 1100 the NTA Na₃ is effective. At about the break point of 1100 p.s.i., effectiveness markedly decreases rapidly with further pressure increase.

The same test was run with respect to EDTA Na₄. The EDTA Na₄ was surprisingly inferior to NTA Na₃ within the pressure ranges of the invention. For example, at a 250 p.s.i. pressure even a three-fold dosage (54 p.p.m. of EDTA Na₄) over that of NTA Na₃ exhibited only 80% scale prevention.

Example II

In another series of tests the effect of the salts of the invention with respect to magnesium phosphate scale prevention was evaluated according to the above described procedure, with the only exception being preparation of feedwater to contain 10 p.p.m. of Mg and 3.0 p.p.m. excess PO₄. These tests were run at a pressure of 800 p.s.i. Results are as follows:

TABLE II

P.p.m.:	Percent scale prevention
30	0
50	90
50	98

The effectiveness of NTA Na₃ on magnesium phosphate scale is apparent. In yet another run 50 p.p.m. of EDTA Na₄ gave only a 75% scale prevention. Again the NTA Na₃ was surprisingly superior at the pressure used in this test.

Example III

In still a further test the NTA Na₃ was evaluated with respect to activity in preventing calcium silicate scale. At a dosage level of 30 p.p.m. the NTA Na₃ exhibited a 75% scale prevention.

Example IV

In this series of runs the effectiveness of NTA Na₃ was evaluated with respect to preventing iron oxide deposition at 400 p.s.i. The make-up water contained 5 p.p.m. of iron as Fe and 3.0 p.p.m. excess PO₄. At a 12 p.p.m. dosage, the NTA Na₃ gave a 85% scale prevention and at 18 p.p.m. a 90% scale prevention.

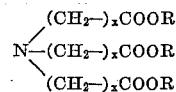
Example V

In a surprising series of tests the effect of variance of heat transfer rate was determined with respect to performances of both NTA Na₃ and EDTA Na₄. The make-up water was dilute Chicago tap containing 5 p.p.m. Ca and 2 p.p.m. of Mg which was subjected to a 800 p.s.i. pressure level in the test described above. At both the 30,000 B.t.u./sq. ft./hr. and 90,000 B.t.u./sq. ft./hr. (heat transfer rates), 36 p.p.m. of NTA Na₃ exhibited a 75% scale prevention. On the other hand, at a 54 p.p.m. level EDTA Na₄ performance at 30,000 B.t.u./sq. ft./hr. was 75% reduction and a surprising 0% reduction at 90,000 B.t.u./sq.ft./hr. or no improvement over blank.

The NTA Na₃ reagent and other salts used in the invention not only demonstrated excellent performance as boiler additives but also did not create a problem of foaming. For example, even a 1000 p.p.m. level treatment of NTA Na₃ in the boiler water did not cause an appreciable increase in the foam level, even in absence of antifoamer. It is understood, of course, that the invention is not limited by the foregoing description and disclosures of the specific examples given hereinabove, which were given solely to illustrate the invention. All modifications which come within the scope and spirit of the appended claims should also be embraced thereby.

The invention is hereby claimed as follows:

1. A method of removing and inhibiting scale formation in boilers in the generation of steam from water which has a tendency to form scale which comprises incorporating with said water from which said steam is generated under pressures ranging from about 250 p.s.i. to about 1100 p.s.i. a quantity of a salt of nitrilotricarboxylic acid sufficient to accomplish said removal and inhibition, said salt having the following structural formula:



where x is an integer of from 1 to 2, and R is a radical selected from the group consisting of hydrogen and alkali metal, with at least one occurrence of R being an alkali metal radical and boiling said water under said range of pressure.

2. The method of claim 1 wherein the pH of said boiling water is at least 9.0.

3. The method of claim 2 wherein said salt is present in an amount of at least 0.1 p.p.m.

4. The method of claim 3 wherein said salt is added to said water in an amount ranging from about 0.1 p.p.m. to about 1000 p.p.m.

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5

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6

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