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PROCESS OF BOILING OUT STEAM BOILERS
PRIOR TO PLACING THEM IN OPERATION
AND COMPOSITION THEREFORWendell W. Cerna, Mount Lebanon, Pa., assignor
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This invention relates to the boiling out of steam boilers prior to placing them in operation for the generation of steam.

It is now common practice to boil out steam boilers with alkaline solutions containing sodium chemicals such as sodium silicate, sodium hydroxide, sodium carbonate, sodium phosphate, or mixtures thereof. The object of this boiling out or cleaning process is to remove oil, dirt, metal cuttings, mill scale and other undesirable materials which are present in the boiler when first constructed. Solid foreign matter should be removed from the new boiler before it is placed in operation in order to prevent danger of interference with the free flow of water through restrictions in the boiler such as tube entrances and orifices. It is advisable to remove the oily coatings because otherwise they would interfere with proper heat transfer, thereby resulting in overheating with consequent damage to the boiler as a whole, or at least to localized areas. Furthermore, if non-mineral oils are not removed before the boiler is placed in operation, saponification of such oily matter results from combination with soluble alkalis in the water used for producing steam, and such saponification results in the formation of soap which induces extreme foaminess of the water. This condition accelerates carryover of liquid from the boiler, which in turn causes considerable damage to auxiliary equipment such as superheaters in boilers, power-generating or power-driven equipment such as steam-driven turbines and pumps, and in certain processes where steam is used, in damage to the product.

As previously mentioned, the chemicals which have been used in the past for cleaning new boilers have always been the sodium chemicals. Sodium silicates, for example sodium metasilicate Na_2SiO_3 , have been used for cleaning out new boilers, the silicates being particularly desirable because of their emulsifying and peptizing effect on oil and grease, their detergent properties and their ability to disperse solid fine particles. Generally, other sodium chemicals have been used along with the sodium silicates to impart other desired properties to the boiling out solution. Although sodium silicate is a very effective detergent, it is almost impossible to flush out the boiler so as to remove all of this cleaning chemical after the boiling out process has been completed. As a result, undesirable concentration of sodium silicate may remain in the boiler after the ordinary boiling out and flushing operations. When the boiler is placed in operation

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to produce steam the high pressures and temperatures cause the formation of sodium silicate scale in the boiler, and in some cases the silica content of moisture carried over with the steam produces sodium silicate deposits on the blades of steam-driven turbines. The deposit of silica scale on the turbine blades reduces the capacity of the turbine, and where the scale is large in amount it is necessary to cut out the turbine and clean it, such as by washing with strong hydroxide solutions or mechanical removal of the scale as by sand blasting.

In accordance with the present invention I overcome the disadvantages resulting from the use of sodium chemicals in boiling out steam boilers. Whereas sodium silicate scale forms in boilers and turbines under the temperatures and pressures there encountered, potassium silicate remains in solution at such temperatures and pressures. By using potassium chemicals or by using chemicals containing a substantial amount of potassium as hereinafter more particularly pointed out for the purpose of boiling out steam boilers, I prevent or inhibit the formation of silicate scale in the boiler or turbine when the boiler is first placed in operation.

The use of potassium chemicals for boiling out steam boilers, instead of sodium chemicals, also minimizes or eliminates deterioration of boiler metal by caustic embrittlement. To produce such embrittlement areas must exist where high concentrations of chemicals can develop, such for example as riveted seams, or rolled-in tube ends. When sodium chemicals are used for boiling out, and silica is present, the sodium silicate tends to form a cement which seals the opening at the outside of the seam and prevents further leakage. As a result, concentration of the chemical solution within the seam may occur until it reaches a concentration sufficiently high to produce metal attack at the grain boundaries. Where, however, potassium chemicals are used, even in the presence of silica, the potassium silicate being soluble does not form a cement under these conditions and therefore does not tend to seal up seams or cause concentration of the chemicals to such an extent that they attack the metal.

The use of potassium chemicals is more especially to be preferred because thereby the primary objective of the boiling out process is more readily attained. It has been observed repeatedly in actual practice that when the boilers are drained and rinsed after boiling out with mixtures including potassium chemicals, the surfaces are consistently free of the occasional oily

patches and the ends of tubes do not show the "tear-drops" present after boiling out with sodium chemicals alone. With potassium ion comprising an appreciable part of the metal ions present in the boiling out solution, the products of saponification of the non-mineral oil and grease are more soluble and the mineral oil and grease are more completely emulsified than when sodium salts only are employed.

There is a wide variety of compositions and solutions which may be employed according to my invention. The solution must be sufficiently alkaline to effectively remove oil and grease. It should contain a silicate because of the detergent properties which silicates possess. There should be a certain maximum ratio of silica to alkali-metal oxide, and a certain minimum ratio of potassium to sodium in order to insure that the silicate formed will be predominantly potassium silicate rather than sodium silicate, thereby producing a soluble silicate rather than an insoluble silicate. The composition used in making the cleaning solution may be made up entirely of potassium chemicals, or of potassium and sodium chemicals, provided it has the required minimum ratio of potassium to sodium.

In order to form soluble silicates rather than insoluble silicates, the ratio of silica to alkali-metal oxide, when expressed in equivalents, should be not more than 1:1, and the ratio of potassium to sodium, when expressed in equivalents, should be at least 0.5:1.

The composition always contains one or more alkali-metal silicates, the preferred range being about 10% to 40% by weight. Although the alkali-metal metasilicates are preferred, I may use alkali-metal silicates having a lower or a higher ratio of alkali-metal oxide to SiO_2 than the metasilicates, provided that the composition as a whole has the proper alkalinity, ratio of silica to alkalinity, and ratio of potassium to sodium. I may use alkali-metal silicates having a mol ratio of alkali-metal oxide to SiO_2 from 2:1 to 1:4. I may use the alkali-metal orthosilicates, sesquisilicates, metasilicates, disilicates, or tetrasilicates. The orthosilicates and tetrasilicates have, respectively, mol ratios of alkali-metal oxide to SiO_2 of 2:1 and 1:4. The other silicates have intermediate ratios. The silicates may be either potassium silicates or sodium silicates, or mixtures of potassium and sodium silicates.

In addition to the silicates the composition preferably contains one or more molecularly dehydrated phosphates which have the property of sequestering calcium. Among the molecularly dehydrated phosphates are the crystalline alkali-metal metaphosphates, pyrophosphates, tripolyphosphates and the alkali-metal phosphate glasses. Either glassy or crystalline molecularly dehydrated phosphates may be employed, provided that they have the property of sequestering calcium under the conditions of use.

The water-soluble crystalline sodium metaphosphate commonly known as sodium trimetaphosphate does not exhibit this property in neutral solution at ordinary temperatures. However, in an alkaline solution it is converted into the calcium-sequestering sodium tripolyphosphate, this conversion being accelerated by increase in temperature. Thus, when sodium trimetaphosphate is used with the alkaline materials required to produce the desired detergent action during boiling out a boiler, sequestration of calcium is developed during the early stages

of the operation by the conversion of the trimetaphosphate to sodium tripolyphosphate.

The water-insoluble crystalline alkali-metal metaphosphates also become effective under the conditions of use. Water-insoluble crystalline sodium metaphosphate is solubilized by potassium salts, and water-insoluble crystalline potassium metaphosphate is solubilized by sodium salts. The insoluble crystalline alkali-metal metaphosphates will even cause each other to go mutually into solution in water, the dissolving action being accelerated by increase in temperature. Since both potassium and sodium salts will usually be present in the water during the boiling out of a boiler according to my invention, the water-insoluble alkali-metal metaphosphates may be employed effectively.

When an alkaline solution is used in boiling out a boiler containing oil or grease, and if the water used in making up the boiling out solution contains calcium, or if calcium is present in the dirt contained in the boiler, the calcium will form insoluble soaps. By the use of a molecularly dehydrated phosphate, the formation of insoluble soaps is prevented until the alkalis present have had an opportunity to react with the oil or grease. Upon continued heating the sodium metaphosphate or other molecularly dehydrated phosphate reverts to the orthophosphate, forming calcium orthophosphate sludge which adsorbs the oil or grease and other foreign material.

The molecularly dehydrated phosphates may be made from potassium salts, sodium salts, or mixtures of potassium and sodium salts, provided the cleaning composition as a whole has the proper ratio of alkali-metal oxide to silica and the proper ratio of potassium to sodium. The molecularly dehydrated phosphate or mixtures of such phosphates in my boiling out composition constitutes about 5% to 50% by weight, and preferably about 10% to 40%. In any event, it should be in amount sufficient to effectively sequester the calcium for a time sufficient to enable the alkaline solution to effectively emulsify any oil or grease that may be present in the boiler which is being cleaned. Where the boiler to be cleaned contains a large amount of oil or grease, it may be found desirable in some cases to add calcium or magnesium salts which are ultimately precipitated in the boiling out process, thereby increasing the amount of precipitate available for adsorbing the oil or grease. Instead of, or in conjunction with, the addition of calcium or magnesium salts, the effect of producing precipitate for oil or grease adsorption may be obtained by using raw water or sea water which naturally contain these calcium and magnesium salts.

In order to increase the alkalinity of the composition strong alkalis such as sodium or potassium hydroxide, orthophosphate or carbonate, may be included. Thus, where the silicate used is the metasilicate, or when any silicate which is less alkaline than the metasilicate is employed, it may be found desirable to include one or more of sodium or potassium hydroxide or carbonate in the composition. Where the orthosilicate is used it may be found that no additional alkali is required. If sodium or potassium hydroxide or carbonate is used it may be used in amount up to about 50% by weight of the composition, for example, in amounts from about 10% to 50%.

Although tripotassium orthophosphate or trisodium orthophosphate are not essential constituents of the composition, they are desirable

ingredients. They form calcium orthophosphate precipitate upon ultimate reaction with the calcium of hard water, this precipitate aiding in adsorbing oil.

If desired, the boiling out composition may contain an inhibitor of embrittlement such, for example, as tannins, lignins, the waste sulphite liquors produced in paper making, or nitrates such as sodium or potassium nitrates, all of which provide additional protection against embrittlement of the boiler metal. Wetting agents which are stable in alkaline solutions may also be included in the chemical mixture for cleaning boilers in order to effect better wetting of surfaces and thus produce better cleaning action by the other chemicals used.

The following are examples of suitable compositions for use according to my invention.

Example No. 1

	Parts
Tripotassium phosphate.....	14
Sodium or potassium molecularly dehydrated phosphate.....	36
Sodium or potassium metasilicate.....	23
Potassium hydroxide.....	27

Example No. 2

	Parts
Trisodium phosphate.....	12
Potassium pyrophosphate.....	38
Sodium metasilicate.....	21
Potassium hydroxide.....	27
Sodium nitrate.....	2

Example No. 3

	Parts
Sodium or potassium molecularly dehydrated phosphates.....	24
Sodium or potassium metasilicate.....	30
Sodium or potassium sesquisilicates.....	6
Potassium hydroxide.....	40

Example No. 4

	Parts
Sodium or potassium molecularly dehydrated phosphate.....	24
Sodium or potassium metasilicates.....	29
Sodium or potassium sesquisilicates.....	6
Potassium hydroxide.....	39
Tannin.....	2

Example No. 5

	Parts
Tripotassium phosphate.....	16
Potassium molecularly dehydrated phosphate.....	38
Sodium metasilicate.....	21
Sodium hydroxide.....	25

Example No. 6

	Parts
Potassium pyrophosphate.....	10
Sodium or potassium molecularly dehydrated phosphate.....	40
Sodium or potassium metasilicate.....	21
Potassium hydroxide.....	27
Sodium or potassium nitrates.....	2

Example 7

	Parts
Sodium or potassium molecularly dehydrated phosphate.....	24
Sodium or potassium metasilicates.....	28
Sodium or potassium sesquisilicates.....	6
Potassium hydroxide.....	38
Calcium hydroxide.....	4

In cleaning a new boiler it is only necessary to heat the cleaning solution to a temperature

sufficient to get circulation, a pressure of about 10 to 150 pounds per square inch generally being sufficient. The compositions are used in an amount of at least 3 pounds per thousand pounds of water in the boiler, which is a concentration of 3,000 P. P. M. Preferably the amount of the composition used is such as to produce a concentration of solids in solution of at least 5,000 P. P. M. up to 10,000 P. P. M., or 20,000 P. P. M. The proportion of alkali in the composition and the amount of the composition used in making the cleaning out solution preferably are such as to produce a cleaning out solution having a caustic alkalinity of from about 100 to about 2500 P. P. M., the caustic alkalinity desirably being not less than 500 P. P. M. The boiler preferably is boiled out for 24 hours or more, although this will vary according to the particular conditions encountered. After the cleaning of the boiler has been completed, the cleaning solution is withdrawn from the boiler and the boiler is flushed out with clean water, after which it is ready to be put into operation for the generation of steam.

The invention is not limited to the examples which have been given merely by way of illustration, but may be otherwise embodied or practiced within the scope of the following claims.

I claim:

1. The process of boiling out steam boilers prior to placing them in operation for the generation of steam, which comprises circulating through the boiler a heated aqueous alkaline cleaning solution having a concentration of solids in solution of at least 3,000 parts per million by weight, said solution containing about 10% to 40% by weight of at least one alkali metal silicate selected from the group consisting of sodium silicate and potassium silicate based on the solids in solution, said solution having a caustic alkalinity of about 100 to about 2500 parts per million by weight, maintaining in said solution a ratio in equivalents of silica to total sodium oxide plus potassium oxide of not more than 1:1 and a ratio in equivalents of potassium to sodium of at least 0.5:1, said circulation being continued until the boiler is effectively cleaned, withdrawing the cleaning solution from the boiler and flushing it out with clean water.

2. The process of boiling out steam boilers prior to placing them in operation for the generation of steam, which comprises circulating through the boiler a heated aqueous alkaline cleaning solution having a concentration of solids in solution of at least 3,000 parts per million by weight, said solution containing about 10% to 40% by weight of at least one alkali metal silicate selected from the group consisting of sodium silicate and potassium silicate based on the solids in solution and from about 5% to 50% by weight of at least one molecularly dehydrated phosphate selected from the group consisting of molecularly dehydrated sodium phosphate and molecularly dehydrated potassium phosphate based on the solids in solution, said solution having a caustic alkalinity of about 100 to about 2500 parts per million by weight, maintaining in said solution a ratio in equivalents of silica to total sodium oxide plus potassium oxide of not more than 1:1 and a ratio in equivalents of potassium to sodium of at least 0.5:1, said circulation being continued until the boiler is effectively cleaned, withdrawing the cleaning solution from the boiler and flushing it out with clean water.

3. The process of boiling out steam boilers prior to placing them in operation for the gen-

eration of steam, which comprises circulating through the boiler a heated aqueous alkaline cleaning solution having a concentration of solids in solution of at least 3,000 parts per million by weight, said solution containing about 10% to 40% by weight of at least one alkali metal silicate selected from the group consisting of sodium silicate and potassium silicate based on the solids in solution and from about 5% to 50% by weight of at least one molecularly dehydrated phosphate selected from the group consisting of molecularly dehydrated sodium phosphate and molecularly dehydrated potassium phosphate based on the solids in solution and an effective amount up to about 50% by weight based on the solids in solution of at least one strong alkali selected from the group consisting of the hydroxides and carbonates of sodium and potassium, said solution having a caustic alkalinity of about 100 to about 2500 parts per million by weight, maintaining in said solution a ratio in equivalents of silica to total sodium oxide plus potassium oxide of not more than 1:1 and a ratio in equivalents of potassium to sodium of at least 0.5:1, said circulation being continued until the boiler is effectively cleaned, withdrawing the cleaning solution from the boiler and flushing it out with clean water.

4. A composition for boiling out steam boilers, comprising by weight about 10% to about 40% of alkali metal silicate selected from the group consisting of sodium silicate and potassium silicate, having a molar ratio of alkali metal oxide to silica between 2:1 and 1:4, and about 5% to 50% of at least one molecularly dehydrated alkali metal phosphate selected from the group consisting of molecularly dehydrated sodium phosphate and molecularly dehydrated potassium phosphate, the ratio in equivalents of silica to total sodium oxide plus potassium oxide in the composition being not more than 1:1, the ratio in equivalents of potassium to sodium in the composition being at least 0.5:1.

5. A composition for boiling out steam boilers, comprising by weight about 10% to about 40% of at least one alkali metal silicate selected from the group consisting of sodium silicate and potassium silicate, having a molar ratio of alkali metal oxide to silica between 2:1 and 1:4, and about 5% to 50% of at least one molecularly dehydrated

alkali metal phosphate selected from the group consisting of molecularly dehydrated sodium phosphate and molecularly dehydrated potassium phosphate and about 10% to 50% of at least one strong alkali selected from the group consisting of the hydroxides and carbonates of sodium and potassium, the ratio in equivalents of silica to total sodium oxide plus potassium oxide in the composition being not more than 1:1, the ratio in equivalents of potassium to sodium in the composition being at least 0.5:1.

6. A composition for boiling out steam boilers, comprising by weight about 10% to about 40% of at least one alkali metal silicate selected from the group consisting of sodium silicate and potassium silicate, having a molar ratio of alkali metal oxide to silica between 2:1 and 1:4, and about 5% to 50% of at least one molecularly dehydrated alkali metal phosphate selected from the group consisting of molecularly dehydrated sodium phosphate and molecularly dehydrated potassium phosphate and about 10% to 50% of potassium hydroxide, the ratio in equivalents of silica to total sodium oxide plus potassium oxide in the composition being not more than 1:1, the ratio in equivalents of potassium to sodium in the composition being at least 0.5:1.

7. A composition for boiling out steam boilers, comprising by weight about 10% to 40% of potassium silicate having a molar ratio of K_2O to SiO_2 between 2:1 and 1:4, about 5% to 50% of at least one molecularly dehydrated sodium phosphate and about 10% to 50% of potassium hydroxide, the ratio in equivalents of silica to total sodium oxide plus potassium oxide in the composition being not more than 1:1, the ratio in equivalents of potassium to sodium in the composition being at least 0.5:1.

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