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WATER TREATMENT TO PREVENT EMBRITTLEMENT CRACKING

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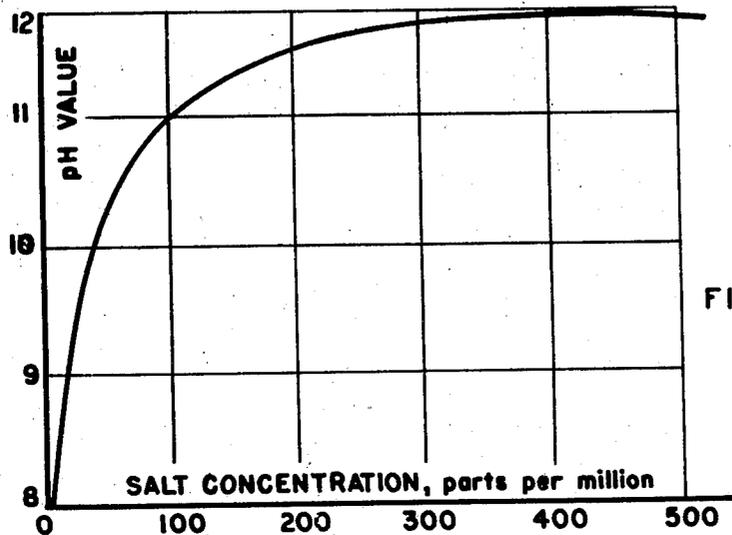


FIG. 1

RELATION OF pH TO CONCENTRATION FOR TYPICAL SALT OF WEAK ACID AND STRONG BASE

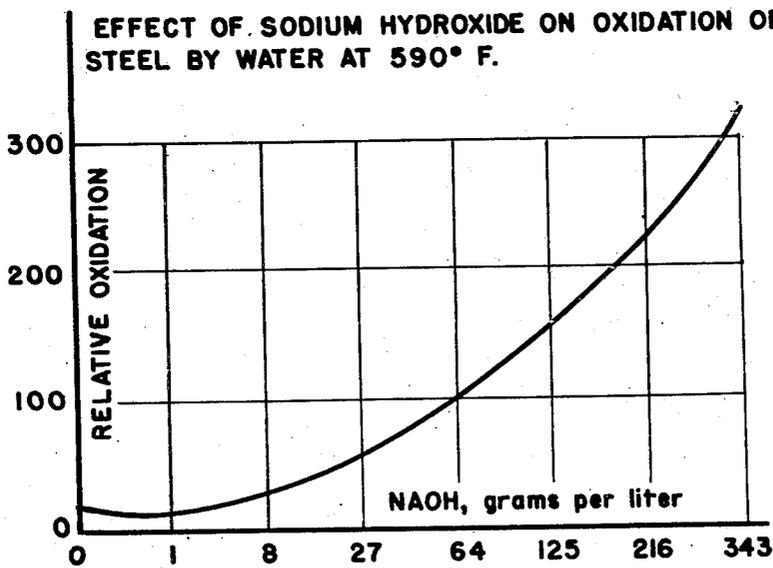


FIG. 2

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# UNITED STATES PATENT OFFICE

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## WATER TREATMENT TO PREVENT EMBRITTLLEMENT CRACKING

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United States of America as represented by the  
Secretary of the Interior

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amended April 30, 1928; 370 O. G. 757)

1

This invention relates to the art of protecting boilers and the like against embrittlement cracking. More specifically, it relates to a method of treating waters, or solutions to be used in boilers and the like, to prevent embrittlement cracking of the steel or other metal with which such waters or solution are in contact.

Boiler waters normally contain a few hundred parts per million of sodium hydroxide and a smaller amount of sodium silicate. Such dilute alkaline solutions have never been shown to produce embrittlement or intercrystalline cracks. In the laboratory solutions containing from 100,000 to 500,000 parts per million of sodium hydroxide and a few hundred parts per million of sodium silicate are necessary to cause cracking. The dilute boiler water can evaporate in small spaces in riveted seams or rolled in tube ends to attain a high concentration of sodium hydroxide such as has been found to cause cracking in the laboratory.

It has been demonstrated that such concentrations can and actually do take place. If the dilute boiler water very slowly leaks or diffuses through a restriction toward a region of lower or atmospheric pressure, the water will tend to evaporate, both because of its superheat and because of the heat supplied from the boiler metal. This will leave a concentrated solution in the region of the restriction. Our work has demonstrated that this process can concentrate a boiler water from 20 to more than 500,000 parts per million of sodium hydroxide.

The behavior of sodium hydroxide in boiler water and its action in causing embrittlement or intercrystalline cracking is more fully disclosed in our Patent No. 2,283,954, granted May 26, 1942; in Patent No. 2,283,955, granted May 26, 1942, to W. C. Schroeder; in our copending application, Ser. No. 237,982, now Patent 2,297,670, granted September 29, 1942, filed October 31, 1938, for Method of protecting boilers and the like against embrittlement; and also in Bulletin 443 of the Bureau of Mines, U. S. Department of the Interior, to which reference may be had for a more comprehensive treatment of this subject as well as for a better and more complete understanding and appreciation of the features and advantages of the present invention.

Certain methods have been suggested in the past that it was believed would eliminate embrittlement cracking in steam boilers. All of these depend on the maintenance in the boiler water of certain ratios between the concentrations of an inhibitor and the boiler water alkalinity, the

2

latter usually being due to the presence of sodium hydroxide and sodium carbonate. It will be seen, therefore, that embrittlement cracking is caused by concentration of the same substances which produce the alkalinity essential to good boiler operation, and that these prior methods of boiler water treatment for the prevention of embrittlement cracking left in the boiler water the sodium hydroxide which is the primary chemical which causes embrittlement cracking. Furthermore, these prior methods depend on the addition to the boiler water of still other chemicals to arrest the action of sodium hydroxide in producing embrittlement cracking. It is highly desirable to avoid the presence in the boiler water of chemicals such as sodium carbonate and sodium hydroxide which can concentrate to cause embrittlement cracking, but it is also important to maintain the requisite alkalinity of the boiler water, as will be understood by those skilled in this art.

Our invention provides for controlling and even for eliminating from the boiler water sodium hydroxide, as well as other dangerous alkalies, and in this way our invention provides for completely eliminating all tendencies of the boiler water to produce embrittlement cracking, while at the same time we provide for maintaining conditions in the boiler water for satisfactorily preventing corrosion.

In the accompanying drawing:

Fig. 1 is a curve relating the pH value at room temperature to the concentration at the equilibrium condition of a salt which may be used in accordance with this invention; and

Fig. 2 is a curve showing the effects of concentrating caustic soda in contact with steel, as a function of the sodium hydroxide concentration, the concentrations being plotted on a cube root scale to adequately include the data.

In our investigation it has been found possible to control the alkalinity so that no matter how many concentrations of the boiler water occur, the concentration of alkali in the water is insufficient to cause embrittlement cracking.

Our work has disclosed that thermally stable salts of strong bases and weak acids in water solution have an alkaline reaction so that the hydrogen ion concentration in water solution is low enough so that waters containing these chemicals may have an alkalinity which makes them satisfactory for boiler use, although there is no other source of alkalinity. It thus becomes possible to eliminate from boiler water those substances which may concentrate to cause embrittlement cracking and also to maintain the desired al-

kalinity for good boiler operation. Furthermore, higher concentrations of the substances used for this purpose in accordance with this invention, such as will result from steaming or evaporation, will not substantially change the alkalinity of the boiler water as would be the case if caustic soda were used to produce the initial alkalinity. And more important, we have found that the highest concentrations obtainable in solutions of the substances provided for this purpose by our invention will not cause embrittlement cracking of boiler steel.

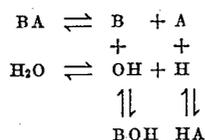
These desirable objectives may be attained in accordance with this invention by simple and preferred modes of procedure as follows:

#### Example 1

(a) Any thermally stable salt of a strong base and a weak acid may be selected, as on the basis of economy, desirability or availability, and may be added to pure water, for example, until the desired alkalinity is obtained. (b) The concentration so found may then be maintained in the boiler water. (c) The absence from the water of free caustic, which could concentrate to cause embrittlement cracking, may be established in various analytical ways, as is well understood by those skilled in this art. (d) If free caustic is found to be present in the boiler water, it should be neutralized by the introduction of a suitable acidic substance until analysis shows that free caustic is no longer present, i. e., until all of the alkali metal hydroxide in the water is at least stoichiometrically balanced by thermally stable weakly acidic radicals.

(a Alternate) The amount of the selected salt to be added to pure water to give the desired alkalinity in accordance with this invention, may also be determined from a knowledge of the equilibria conditions for this salt and pure water.

As is well known, water is not an inert matter and the process of solution of substances in water is often accompanied by chemical reaction. The alkalinity of a solution of a salt of a strong base and a weak acid is recognized to be due to such an interaction with water. Thus:



The double arrows are employed in their usual sense, i. e., they denote a complete reversibility of the system. BA represents the salt of a weak acid HA and a strong base BOH, wherein either A or B or both may be a complex radical with any valence.

The reaction illustrated is taken from the textbook "Outlines of Theoretical Chemistry," by Getman and Daniels, 6th edition, 1937, John Wiley and Sons, and is typical for salts formed from a weak acid and a strong base. The process is called hydrolysis and in the illustration is due to the removal of the hydrogen ion by the ions of the salt to form a relatively undissociated substance. As fast as the ions of water are removed, the loss is made good by the dissociation of more water until, eventually, a condition of equilibrium is established.

It will be noted from these equations that when the water is removed from a system containing only water and BA, only BA is formed and there is no formation of a strong base BOH, such as caustic soda. In this specification the term free

caustic is used to denote any BOH in excess of that derived from such hydrolysis and which may therefore concentrate to form a strongly alkaline solution when the water is removed by steaming or evaporation.

The conditions governing hydrolytic equilibrium may be determined from a knowledge of the solubilities and ionization constants of the substances involved. Thus, if the product of the concentrations of the ions H and A exceeds that which can exist in the solvent, then some undissociated or insoluble substance is formed. This disturbs the equilibrium of H and OH ions, and a further dissociation of water occurs, until the ionic product of water is just reached. A similar readjustment will take place with respect to each undissociated or insoluble substance present in the water.

The room temperature constants for the equilibria pertinent to most substances present in boiler waters are well known. McKinney ("Calculations for Corrections to Conductivity Measurements for Dissolved Gases," by D. S. McKinney, Proc. American Society for Testing Materials, p. 1285, vol. 41 (1941)) has shown how these several substances are interrelated. Through the use of his method, it is possible to calculate the equilibria in dilute solutions such as are represented by boiler waters. For convenience, all such calculations may be and herein are based on room temperature conditions. From a knowledge of the concentrations of dissolved substances, the hydrogen ion concentration can be computed. Conversely, the distribution of the electrolytes in solution can be calculated as a function of the hydrogen ion concentration. It is, therefore, unnecessary to measure the alkalinity produced by a selected salt of a strong acid and a weak base when the constants pertaining to its equilibria with water are known. The amount required to give to the water a desired alkalinity may be calculated and this concentration maintained in the boiler water.

#### Example 2

Another preferred mode of practicing this invention involves the determination of the pH value of the boiler water. (a') Any thermally stable salt of a weak acid and a strong base may be selected and added to pure water as previously described herein. The pH values at equilibrium conditions for any given number of concentrations of the selected salt in pure water may then be determined and a curve plotted relating the concentrations to the pH values. A curve of this kind is illustrated in Figure 1. (a' Alternate) If desired, such a curve may also be calculated from the known constants. The points on such a curve representing pH values for optimum boiler operating conditions will also represent the concentrations of the selected salt which will give these pH values. In this manner, the range of concentrations of the selected salt to be maintained in the boiler water to give the desired pH range may be obtained, assuming the absence of free caustic from the boiler water. For satisfactory operation and protection against corrosion and scale, the boiler water should be maintained at a pH value of 8.5 to 12 and preferably at a pH value of 10 to 11.

(b') In using a curve of the kind just described, the concentration of the selected salt, corresponding to the desired pH value on the curve, may be produced and maintained in the boiler water on the basis of chemical analysis. As long

5

as the pH value for the boiler water so treated and the concentration therein of the selected salt conform to this curve, only the selected salt can be formed when the water is evaporated. In other words, under these conditions the selected salt may be termed a "captive alkali" since on evaporation all the alkalinizing metal is recaptured as the salt.

If any free caustic should be present in the boiler so that evaporation would produce a concentrated solution of caustic soda, the pH of the boiler water would necessarily be above the curve value corresponding to the concentration of the selected salt. (c') If "free caustic" is so found to be present in the boiler water, it should be neutralized by the introduction of a suitable acidic substance until the pH conforms to the curve value. As indicated above, sodium carbonate is a source of alkalinity. It is thus obvious that carbonic acid would not be a suitable acidic substance, since it would not eliminate free caustic by forming therewith a salt stable at boiler temperatures. As indicated at page 65 of Bulletin 443, referred to above, when trisodium phosphate is employed as the captive alkali, an acid phosphate, as an alkali dihydrogen phosphate, is a suitable acidic substance. And as mentioned hereinafter, the secondary phosphate may be employed with the tertiary phosphate. In either case, this is equivalent to addition with a quantity of the "captive" alkali (BA in the equilibrium equation above) of a quantity of the corresponding acid (HA therein), which by reaction with concentratable NaOH (i. e. caustic in excess of the BOH of the equation) effectively eliminates it from the system. When enough neutralization is effected the pH will be reduced to the value of the curve (Fig. 1); when some excess of the acidic substance is introduced, the pH of the boiler water will lie below the curve. To afford complete protection against embrittlement, the measured pH should never be above the value from the curve and when this condition prevails all of the alkali metal hydroxide in the water is at least stoichiometrically balanced by thermally stable weakly acidic radicals so that no concentrated caustic can be formed when the water is evaporated. As above pointed out, boiler water containing as little as 20 P. P. M. of free NaOH supplied to a seam which leaks over a substantial period of time, can concentrate in time to more than 500,000 P. P. M. of NaOH. Therefore, for complete protection we prefer to always maintain a "zero-free caustic" condition. However, as noted in Bulletin 443, above cited, we were not able to produce cracking of test specimens in tests where the unconcentrated water contained 20 P. P. M. of free NaOH or less, presumably because the loss of NaOH from the seams, for example as carry-over in the vapor, tended then to become as great as the rate of supply of NaOH from the extremely dilute boiler solution. Thus, our experiments indicate that a very small concentration of free caustic can be tolerated at least for short times without causing embrittlement cracking. This free caustic as a practical matter should never be more than 20 parts per million expressed as sodium hydroxide or over 0.2 pH unit above the curve value corresponding to the concentration of the selected salt when the curve value is between 10 and 12.

If the pH should fall below the curve, representing a stoichiometrical excess of weak acid,

6

no substance will be formed which can cause embrittlement, but the selected salt is no longer being used to full advantage to produce the desired alkalinity. If the pH value is below the curve value corresponding to the concentration being maintained of the selected salt, the desired alkalinity may be restored by adding caustic soda or other suitable alkaline substance, as will be understood by those skilled in this art.

It will be seen from Equation 1 that so long as the pH value is not above the curve value corresponding to the concentration of the selected salt, the caustic soda so added does not become free caustic such as on evaporation would form a concentrated solution which would cause embrittlement cracking, for the curve value represents the equilibrium conditions at which all the alkalinity present is derived from the selected salts, i. e. is "captive" alkalinity which on evaporation of the water is recaptured in the form of salt, and does not remain as free caustic.

#### Other advantages

An important advantage of this method of conditioning water for boiler use lies in the fact that the total solids in water so treated are not materially increased by the treatment, since no embrittlement inhibitor is added and a minimum of chemicals are added to evaporated make-up such as is commonly used in high-pressure installations. The blowdown requirements to restrict the concentration of total solids in the water so as to minimize carry-over of such solids in the steam are materially decreased. There is, therefore, a resultant economy both from the energy bound up with the very hot water discarded and the chemicals in that water.

A further advantage of this method of conditioning water for boiler use lies in the fact that since solids evaporated from such water contain no free caustic soda, such solids when deposited on turbine blades will not form a sticky deposit of sodium hydroxide. Since the latter deposit acts as a binder for other solids in the steam, it will be seen that in the absence of caustic, turbines can be run more efficiently for longer periods without uneconomical outages for cleaning.

A further advantage of this method of conditioning water for boiler use lies in the fact that caustic soda concentrated in contact with hot metal presents a serious corrosion hazard. Figure 2 (from Berl and Van Taack, *Forschungsarbeiten auf dem Gebiete des Ingenieurwesens*, 330, 1930) shows how sodium hydroxide effects the oxidation of steel by reaction with water at 590° F. (the temperature of many modern high-pressure installations). Partridge and Hall ("Attack on Steel and High Capacity Boilers as the Result of Overheating Due to Steam Blanketing," by E. P. Partridge and R. E. Hall, *American Society of Mechanical Engineers*, trans., p. 597, 1939) have shown that even in the more modern boilers operated at this temperature and pressure, the boiler tubes may tend to run dry so that they contain steam rather than water. The boiler water, therefore, evaporates in contact with the hot steel of the tubes. When the water is treated with caustic soda, this chemical concentrates on the tube surfaces and causes rapid deterioration of the metal, resulting in serious corrosion and a consequent hazard to life and property. When the boiler water is adjusted in accordance with this invention so that no concentrated solutions

of caustic soda are formed if evaporation takes place, no such corrosion hazard is presented in tubes that at times run dry.

#### Variations

Any thermally stable salt of a strong base and a weak acid that has the property of increasing the pH of water without supplying to it free caustic which would concentrate when the water is evaporated, may be used for the purposes of this invention. The fluorides, acetates, silicates, chromates, arsenates, secondary and tertiary phosphates, citrates, and borates of the metals of the alkali metal group are fairly representative of the salts that may be selected. However, we prefer to use secondary and tertiary alkali phosphates, either separately or together, notably secondary and tertiary sodium phosphates, as these substances are very effective for the purpose of this invention and their use has been found to give highly satisfactory results. Thus we prefer to neutralize concentratable NaOH with the acid corresponding to the salt selected as the captive alkalizer, which in this instance is added in the form of secondary phosphate. This is preferred since it aids in maintaining the selected concentration of the alkalizer despite dilution from carry over, blow down and sampling, but it is obvious that other acids which effectively eliminate the free caustic may be employed.

All of these substances will each have its own curve to show relationship between its concentration and the resultant pH in water. In some cases, the character of these curves will be such as to restrict the use of the chemicals to particular purposes requiring especially low or especially high alkalinities. It must be emphasized that by maintaining such solids in specified concentrations in boiler water containing no other source of alkalinity, definite conditions of pH are fixed so that when the pH is below such a fixed value, concentration of the boiler water will not result in the formation of concentrated sodium hydroxide in the water and no embrittlement cracking will result.

The terms "strong" and "weak" as applied to acids and bases herein and in the claims, refer to the conductivity or the degree of ionization in aqueous solutions of moderate dilution. Strong bases and acids are distinguished from weak ones by their extensive dissociation in water solution, which is practically complete even at moderate concentrations. When a salt is said to be formed from a strong base and a weak acid, the dissociation constant of the base is much greater than the dissociation constant of the acid. Mellor, "Modern Inorganic Chemistry," p. 372, Longman's, Green and Company, 1925, Getman and Daniels, "Outlines of Theoretical Chemistry," 6th edition, 1937, John Wiley and Sons.

The invention described herein, if patented, may be practiced, manufactured and used by or for the Government for governmental purposes without the payment to us of any royalty thereon.

It should be understood that the present disclosure is for the purposes of illustration only, and that this invention includes all modifications and equivalents which are within the scope of the appended claims.

We claim as our invention and desire to secure by our patent:

1. A method of conditioning the water in a boiler to render it alkaline but incapable of

yielding strong concentrations of caustic soda on evaporation, in which the alkalinity is imparted to the water exclusively by hydrolytic dissociation of alkali-metal salts and especially one of said salts selected from the group consisting of secondary and tertiary phosphates, silicates, borates, acetates and fluorides, and in which the alkalinity of the boiler water is controlled by determining the concentrations of all the alkali-metal salts of said group contained in the boiler water exclusive of the selected salt and determining the concentration of the selected salt which in conjunction therewith would impart to pure water a selected pH value desirable for boiler operation and lying between 8.5 and 12, adding to the boiler water the so determined concentration of the selected salt, testing the pH of the boiler water from time to time, and adding thereto such quantities of the selected salt and of acid and basic agents as are indicated by the tests to be necessary concurrently to maintain the so determined concentration of the selected salt and an alkalinity of the boiler water between the selected pH value and 3.5.

2. A method according to claim 1, in which the selected pH value lies between 10 and 11.5.

3. A method according to claim 1, in which the selected salt is tri-sodium phosphate.

4. A method according to claim 1, in which the selected pH value lies between 10 and 11.5 and in which the selected salt is tri-sodium phosphate.

5. A method according to claim 1, in which the selected salt is tri-sodium phosphate, and in which the adjustment of alkalinity is effected in part at least by addition of an acid sodium phosphate, whereby the adjustment is effected concurrently with variation of the concentration of sodium phosphate in solution, within the pH limits set forth.

6. The method of treating boiler water which consists in maintaining in the boiler water a concentration of at least one thermally stable salt of a strong base and a relatively weak acid, which salt concentration, if maintained in otherwise pure water, would impart to the pure water a definite pH value lying between 8.5 and 12, testing the pH of the boiler water from time to time, and adding thereto a caustic-neutralizing acidic agent which forms a thermally stable salt with the metal of the caustic to reduce its pH to said definite value when the test shows its pH rising above said value.

7. The method of treating boiler water which consists in maintaining in the boiler water a concentration of at least one thermally stable salt of a strong base and a relatively weak acid, which salt concentration, if maintained in otherwise pure water, would impart to the pure water a definite pH value lying between 8.5 and 12, testing the pH of the boiler water from time to time, adding thereto an alkaline substance to raise its pH to said definite value when the test shows its pH to be dropping materially below said value, and adding thereto a caustic-neutralizing acidic agent which forms a thermally stable salt with the metal of the caustic to reduce its pH to said definite value when the test shows its pH to be rising above said value.

8. The method of treating boiler water which consists in maintaining in the boiler water a concentration of alkali metal phosphate which, if maintained in otherwise pure water, would impart to the pure water a definite pH value lying between 8.5 and 12, testing the pH of said boiler water from time to time, adding caustic

alkali thereto to raise its pH to said definite value when the test shows its pH to be dropping materially below said value, and adding thereto an acidic agent which forms a thermally stable salt with the metal of the caustic to reduce its pH to said definite value when the test shows its pH to be rising above said value.

9. The method of treating boiler water which consists in maintaining in the boiler water a concentration of tri-sodium phosphate which, if maintained in otherwise pure water, would impart to the pure water a definite pH value lying between 8.5 and 12, testing the pH of said boiler water from time to time, adding sodium hydroxide thereto to raise its pH to said definite value when the test shows its pH to be dropping materially below said value, and adding thereto an acidic agent which forms a thermally stable salt with the metal of the caustic to reduce its pH to said definite value when the test shows its pH to be rising above said value.

10. A method according to claim 9, in which the added acidic agent is selected from the group consisting of phosphoric acid and acid sodium phosphates.

11. The method of treating boiler water which consists in maintaining in the boiler water a concentration of a thermally stable alkali metal salt of a relatively weak acid, which salt concentration, if maintained in otherwise pure water, would impart to the pure water a definite pH value lying between 8.5 and 12, testing the pH of the boiler water from time to time, adding thereto an alkali substance to raise its pH to said definite value when the test shows its pH to be dropping materially below said value, and adding thereto a caustic-neutralizing acidic agent which forms a thermally stable salt with the metal of the caustic to reduce its pH to said definite value when the test shows its pH to be rising above said value.

12. A method according to claim 6 in which the added acidic agent comprises an acid which combines with free caustic to form the first mentioned thermally stable salt, so that its addition concurrently eliminates free caustic and aids in maintaining the concentration of said salt.

13. The process of protecting boiler metal from caustic attack which comprises employing as the boiler water a solution consisting essentially of tri-sodium phosphate and water, testing the solution to determine whether it contains free hydroxide of an alkali metal in excess of that of a pure aqueous solution of tri-sodium phosphate of equal phosphate concentration, and adding to the boiler water solution as needed a sufficient quantity of an acid phosphate to neutralize said free hydroxide.

14. The process of protecting boiler metal from caustic attack which comprises operating the boiler with a boiler water solution consisting essentially of tri-sodium phosphate and water, testing the boiler water solution to determine whether it contains free hydroxide of an alkali metal in excess of that of a pure aqueous solution of tri-sodium phosphate of equal phosphate concentration, and adding to the boiler water solution as needed a sufficient quantity of an acidic substance to neutralize said free hydroxide.

15. The process of protecting boiler metal from caustic attack which comprises operating the boiler with a boiler water solution consisting essentially of water alkalized with a thermally

stable salt of a strong base and a relatively weak acid, testing the solution to determine whether it contains free hydroxide of an alkali metal in excess of that of a pure aqueous solution of said salt of equal acid radical concentration, and adding to the boiler water solution as needed a sufficient quantity of an acidic substance to neutralize said free hydroxide.

16. The method of protecting boiler metal from caustic attack which comprises operating the boiler with a boiler water consisting essentially of an aqueous solution of tri-sodium phosphate which contains no free hydroxide of an alkali metal in excess of that of a pure aqueous solution of said phosphate of equal phosphate concentration.

17. The method of protecting boiler metal from caustic attack which comprises operating the boiler with a boiler water consisting essentially of an aqueous solution of a thermally stable salt of a strong base and a weak acid which contains no free hydroxide of an alkali metal in excess of that of a pure aqueous solution of said salt of equal acid radical concentration.

18. The method of protecting boiler metal from caustic attack which comprises operating the boiler with boiler water consisting essentially of an aqueous solution of tri-sodium phosphate including a small proportion of disodium phosphate.

19. The method of protecting boiler metal from caustic attack which comprises operating the boiler with boiler water consisting essentially of an aqueous solution of a thermally stable salt of a strong base and a weak acid including a small proportion of a thermally stable caustic neutralizing acidic agent.

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