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PREVENTION OF EMBRITTLEMENT

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This invention relates to the treatment of steam boiler water in order to prevent the occurrence of embrittlement in steam boilers. The process of the invention is particularly applicable to the treatment of waters in boilers being fed with waters relatively low in scale forming elements, such as calcium and magnesium, also having sulfate content low in respect to the soda alkalinity, and which operate at relatively high pressures.

A large percentage of boiler feed waters contain sodium alkalinity which occurs either naturally or as the result of water treatment. The presence of the sodium alkalinity, either as a bicarbonate, carbonate, or hydrate, is desirable in order to prevent corrosion due either to acidity or other causes, to precipitate scale forming ingredients, and to reduce the total solids in the feed water.

When the water containing sodium carbonate or bicarbonate alkalinity enters the boiler, it is partially converted to hydrate alkalinity, the carbon dioxide going off with the steam. This conversion is dependent upon the amount of carbonate entering the boiler, the temperature of the boiler water (steam pressure), and the rating at which the boiler operates. At higher pressures with lower makeup, the conversion becomes as high as 90 per cent. The resultant alkalinity, if not too high, is desirable within the boiler since it has certain beneficial effects in retarding corrosion and preventing scale formation.

We have found that this causticity or sodium hydroxide is the cause of the cracking of rivets and steel plates of boilers in the vicinity of the seams in steam boilers. This cracking has been commonly referred to as "embrittlement" or "caustic embrittlement" of boiler plates. For years this difficulty could not be stopped, and very little was known as to the cause. We have slowly accumulated data which proves conclusively that the sodium hydroxide in the boiler is the offending agent and the cause of the embrittlement. We have found that the crack occurring in the boiler steel is of a distinct type which is not common to mild steel, being intercrystalline in nature. Thus, apparently, the crystal boundaries have become weakened and the metal fractures free from evidence of ductility.

We have devised a testing machine which simulates the conditions existing in the seams of a steam boiler and by means of this testing machine we have been able to make normal boiler steel crack in the same manner in which the so-called embrittlement cracking takes place in the steam boiler, intercrystalline and without evidence of ductility. We have found that sodium hydroxide is the only chemical occurring in the normal boiler waters which will cause this particular cracking of the steel under tension. A complete description of our findings in this respect appears in Bulletins 155 and 177 of the Engineering Experiment Station of the University of Illinois, to which reference may be had for a more complete explanation of the principles involved.

In order to facilitate an understanding of our invention, a brief description of the mechanism of embrittlement will be given. The steel of the boiler has a definite electromotive force in respect to the sodium hydroxide within the boiler seams. If this E. M. F. is sufficient, the iron is attacked with the evolution of hydrogen and the formation of a coating of Fe_3O_4, magnetic oxide, on the steel. The E. M. F. of the steel coated with this oxide is low in respect to the caustic solution, which favors penetration. The steel under strain has the grain boundaries under high stress which adds to the already more chemically active property and accelerates penetration at these points.

From all the data available the following very brief and partially incomplete explanation is made at this time to account for this particular cracking.

The main essential is a solution which has an E. M. F. with respect to steel just sufficient to favor the reaction:

$$3Fe+4OH=Fe_3O_4+4H$$

The E. M. F. should not be any higher than necessary to start this reaction at the temperature involved. When the metal is in an unstrained condition, a thin compact coat of

oxide is formed which is slowly penetrated with the forming of a heavier coat. The attack is fairly even and penetrates the metal at an even rate at all points.

If the metal is subjected to sufficient stress under these conditions the grain boundaries become active, first, from the increased chemical activity brought about through the energy stored up there by the stress, and second, by an increased E. M. F. produced at these points of high stress. If the electromotive force is just sufficient to favor the action on the metal, this slight increase at the grain boundaries becomes sufficient to favor a much more rapid penetration at this point. The products of the action Fe_3O_4 and H_2 both tend to favor the further penetration. As already pointed out by Williams and Homerberg (Transactions, Am. Soc. Steel Treating, April, 1924), the hydrogen thus liberated will penetrate into the fine capillaries at the grain boundaries and reduce the impurities there existing, weakening the bond along such boundaries.

It has been found that sodium sulphate, if present in the boiler water in sufficient quantities, prevents the embrittlement of the boiler plate. The influence of sodium sulphate is easily explainable on this basis. Sodium carbonate behaves in a similar manner. The salt crystallizing out forms a saturated solution on the immediate surface of the metal, lowers the E. M. F. of the metal, and stops the action. It may be a plugging effect, thus keeping the solution away, or, the salt may play the role of a buffer solution, or an insulator, lowering the E. M. F. Oxidizing solutions like chromates will produce this effect. The phosphates, acetates, carbonates, and tannates all act as buffers and modify or eliminate the action.

The results of the experimental work show that boiler plate when stressed below the region of the yield point will not crack when subjected to caustic attack. To think of stresses in boilers in the range of the yield point of boiler plate should not necessarily conflict with our ideas in regard to construction of boilers. It has been common knowledge for years that there are high concentrated stresses in the riveted areas of boilers. Thousands of boilers have operated with these stresses present until discarded. This is due to the fact that a ductile metal like boiler plate can endure localized stresses of this magnitude indefinitely. Naturally, it is well for the boiler manufacturer to reduce these stresses to as low a figure as possible.

The concentration curves show that cracking can take place at much lower concentrations than heretofore predicted, and over a period of long duration one might expect to encounter cracking if the caustic concentration reaches approximately 4000 grains per gal. This is but twenty times the actual concentration which is sometimes reached in the boiler. Seams with small crevices between the plates, under the high temperature and pressure incident to boiler operation, and with small incipient leaks which act as reducing valves and allow the liquid to flash out as steam leaving the salts behind, cause the solution to concentrate. Thiel has shown that these concentrations may reach as high as 75 per cent NaOH in the seam of a boiler. Tests conducted in our laboratory have shown the possibility of a solution of 200 grains of caustic per gal. being concentrated in a space between two cylinders to 7000 grains and still be in contact by means of a leak between the inside and outside with the original solution of 200 grains.

It has been recommended by the American Society of Mechanical Engineers that sodium sulfate be maintained at a definite ratio in respect to the soda alkalinity in the boiler water. This ratio varies depending on the pressure. Up to 150 pounds, this is 1:1; up to 250 ponds it is 2:1; and above 250 pounds, it is 3:1. The operators of higher pressure boilers are using higher ratios so that at 600 pounds pressure a ratio as high as 7:1, or 8:1 is being maintained.

In order to decrease this ratio in boiler feed water various methods have been used. The water has been partially neutralized with sulphuric acid, or iron or aluminum sulphate. Sodium acid sulphate has also been used as well as sodium sulphate. There is much objection to the use of acids, since an overdose would cause much corrosion. Corrosion also results in the equipment used for acid treatment even under excellent control. The use of sulphate salts increases the solids to such an extent as to make undesirable its use for higher steam pressures. In the case of evaporators to supply distilled water makeup, quite often a water containing sodium alkalinity is fed to the evaporators and with a small carrying over or priming these sodium salts reach the boiler. The alkalinity of the evaporated water is too low to be acid treated, and the addition of sulfate salts would defeat the purpose of evaporation. Consequently, there is need for inhibitants other than the sulfate.

The inhibitant used must be effective to prevent embrittlement and must behave in a satisfactory manner for use in boilers. The inhibitant must be such that a minimum amount of solid matter is introduced into the boiler. We have found that phosphate salts satisfy both requirements in that they prevent embrittlement taking place and the quantities of phosphate involved are so small as to be unobjectionable.

In order to use this method in power plants it becomes obvious that we must introduce the phosphate in the boiler or the boiler feed water in such form that the phosphate will exist in the boiler water as the soluble phosphate. Furthermore, it must be present in

definite amounts determined by the sodium alkalinity of the boiler water.

In our actual boiler tests where we use phosphate to prevent embrittlement we prefer to add the phosphate as the sodium salt, but we can add it as the conosodium, disodium, trisodium, or even as phosphoric acid. The addition of the phosphate in any form which will produce a soluble phosphate in the boiler water is suitable for the prevention of embrittlement.

Since soluble phosphate will react with calcium or magnesium under certain conditions and precipitate out as the insoluble salts of these elements, it is preferred to use this method after primary treatments such as the base exchange or the lime soda to save in cost of chemical and make a more effective control. We prefer to use the phosphate in such amounts that it shall not be less than 1/50 of the total alkalinity of the boiler water. We refer to phosphate always as the radical PO_4, though it may be calculated in other combinations if desirable. Due to the fact that the introduction of calcium and magnesium may precipitate the phosphate, we prefer to use the phosphate in the desired ratio to the alkalinity but to also maintain a minimum amount for a protection against this possible loss and also to keep within the limits of accurate determination. This minimum value we would recommend to be about 35 parts per million of PO_4. Thus, if the alkalinity is below 1750 parts per million, at least 35 parts per million of phosphate should be maintained in the boiler water; if above this value, maintain 1/50 of it as PO_4.

Where a low makeup of treated water is used at 600 pounds pressure with the sulphate too low to meet the A. S. M. E. requirements, we have found that between 50 and 70 parts per million of phosphate is the amount to be recommended. In another case using evaporators it would be desirable to maintain about 50 parts per million of PO_4. The lower limit of about 35 parts per million is recommended because this is the lowest concentration which can be readily determined by the operators with any degree of accuracy. Also, if some calcium is present it will precipitate the phosphate and it is therefore essential to have a slight excess of phosphate present to prevent the removal of the phosphate by the calcium. The upper limit is set merely to prevent waste of chemicals since larger amounts of phosphate will not cause any difficulty beyond increasing the cost and the total solids in the boiler. In some plants where the control is not very accurate, a larger excess of phosphate might be desirable.

We prefer the phosphate treatment since an overtreatment with the phosphate in any form but the acid or acid salt will not cause corrosion, it will not cause large increases in total solids, and its use is more economical, especially as a secondary treatment after primary softening.

In some instances it may be desirable to control the use of phosphate by the sodium hydroxide alkalinity in preference to the total sodium alkalinity.

The results of tests on the use of phosphates in boiler waters indicate that comparatively small amounts of this radical will retard the embrittling action of sodium hydroxide. Thus as low as 0.6 grams per liter of phosphate radical (PO_4) prevents embrittlement in the presence of 280 grams per liter of sodium hydroxide, at a steam pressure of 500 pounds per square inch. The phosphate radical appears to be about 150 times as effective as the sulphate.

We have also found as a result of extensive tests that nitric salts have a pronounced inhibiting effect upon the embrittlement action. The salt used was sodium nitrate ($NaNO_3$) and it was found that very small quantities of this salt were effective to stop the embrittlement action. It would thus appear that the phosphates and the other related compounds of the same chemical family will act to prevent or retard the embrittlement of the boiler plate.

As previously stated, we have found that the chromates, tannates, acetates, carbonates, etc. are also effective to inhibit embrittlement. At a boiler pressure of 500 pounds per square inch, approximately 10 grams of tannate must be used to produce an inhibiting effect equal to that produced by one gram of phosphate, or 75 to 100 grams of acetate must be used to produce that same inhibiting effect. While the effectiveness of the tannates or the acetates is a good deal less than that of the phosphates, they are still a good deal more effective than the sulfates.

The following tables indicate the effect of phosphate, tannic acid and sodium acetate in inhibiting embrittlement of flange steel such as is used on boilers. The stress on the specimens used was 45,000 pounds per square inch and the steam pressure was 500 pounds per square inch.

I

Phosphate as an inhibiting agent

Concentration of sodium hydroxide solution—grams per liter	Amount PO_4 radical in solution—grams per liter	Time of cracking—hour	Ratio PO_4 to alkalinity as sodium carbonate	Ratio PO_4 to alkalinity as sodium hydroxide
295	0	24	0.0	0.0
280	0.4	20	0.0010	0.0014
280	0.6	No crack in 13 days	0.0015	0.0021
280	0.6	No crack in 30 days	0.0015	0.0021
280	1.0	No crack in 13 days	0.0025	0.0035
280	1.0	No crack in 17 days	0.0025	0.0035
280	2.0	No crack in 13 days	0.0050	0.0070

II

Tannic acid as an inhibiting agent

Concentration of sodium hydroxide solution—grams per liter	Amount tannic acid added, to solution—grams per liter	Time of cracking—hour	Ratio tannate to alkalinity as sodium carbonate	Ratio tannate to alkalinity as sodium hydroxide
250	0	20	0.0	0.0
275	5	20	0.013	0.018
290	10	No crack in 30 days.	0.024	0.034
290	10	No crack in 20 days.	0.024	0.034
275	15	No crack in 30 days.	0.090	0.120
270	50	No crack in 10 days.	0.130	0.185

III

Sodium acetate as an inhibiting agent

Concentration of sodium hydroxide solution—grams per liter	Amount sodium acetate in solution—grams per liter	Time of cracking—hour	Ratio—sodium acetate to alkalinity as sodium carbonate	Ratio—sodium acetate to alkalinity as sodium hydroxide
280	0	20	0.0	0.0
290	20	28	0.050	0.069
285	50	42	0.125	0.175
285	75	No crack in 25 days.	0.188	0.263
290	100	No crack in 20 days.	0.246	0.345

The term "boiler" as used herein is intended as a term of general definition and is intended to include all devices wherein water is heated to its boiling point.

In compliance with the requirements of the patent statutes we have herein described a few preferred embodiments of our invention. The invention is, however, not limited to the precise embodiments described. What we consider new and desire to secure by Letters Patent is:—

1. The method of preventing embrittlement of boiler metal which comprises maintaining in the boiler a soluble phosphate compound in amounts so that the PO_4 content shall be equal to about 2% of the total alkalinity of the boiler water.

2. The method of preventing embrittlement of boiler metal which comprises maintaining in the boiler sodium phosphate in amounts less than about 4% of the total alkalinity of the boiler water.

3. In a high pressure boiler containing water which is free of substantial amounts of calcium and magnesium and which contains sodium alkalinity and is free of sulphates to an appreciable extent of the sodium alkalinity, the method of preventing embrittlement of the boiler plate which comprises maintaining in the boiler water a phosphate in amounts substantially less than twenty per cent of the sodium alkalinity.

In witness whereof, we hereunto subscribe our names this 22 day of May, 1929.

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