Patented May 11, 1943 2,318,663

# UNITED STATES PATENT OFFICE

2,318,663

## COMPOSITION AND METHOD FOR TREATING BOILER WATER TO PREVENT CAUSTIC EMBRITTLEMENT

Paul G. Bird, Western Springs, and Wilson Evans, Hinsdale, Ill., and Carlyle Harmon and Jörgen Richter Salvesen, Wausau, Wis., assignors to Marathon Paper Mills Company, Rothschild, Wis., a corporation of Wisconsin, and National Aluminate Corporation, Chicago, Ill., a corporation of Delaware, jointly

No Drawing. Application March 4, 1941, Serial No. 381,762

13 Claims. (Cl. 210—23)

This invention relates to the treatment of boiler water to prevent caustic embrittlement or intergranular attack of steel boiler plates.

The invention consists in the discovery that caustic embrittlement of steel boiler plates can be prevented by adding to the normal boiler water a combination of chemicals consisting of a sufficient minimum amount of sodium sulphite, or its equivalent, and a sulphonated organic substance of suitable colloidal character and which has the property of preventing or retarding the oxidation of the sodium sulphite, such as lignin sulphonate.

The exact mechanism taking place in steel boiler plates undergoing caustic embrittlement is not well established. It is known that failure occurs only in plates under great mechanical stress when in contact with caustic soda solution of the order of 20,000 to 40,000 parts per million, together with a small amount of sodium silicate. In order to obtain such a high concentration of caustic it is necessary that a small leak exist so that the boiler water may escape very slowly. As the water evaporates around such a leak it concentrates and deposits caustic soda, sodium sulphate and other dissolved materials present in the water.

Previous attempts to prevent caustic embrittlement were based on maintaining in the boiler water a certain ratio of sodium sulphate to total alkalinity. The A. S. M. E. code recommends that for boiler pressures up to 150 lbs., one part of sodium sulphate be maintained for each part of total alkalinity, expressed as sodium carbonate present in the water. For pressures from 150 to 250 lbs. the recommended ratio is increased to two parts of sodium sulphate for each part of caustic, and for pressures greater than 250 lbs. the recommended ratio is increased to three parts. It is known that caustic embrittlement takes place even when these recommended ratios are maintained. It was this fact, and the difficulties encountered in maintaining such ratios that led us to seek a successful solution of the problem of preventing caustic embrittlement.

In general, boiler waters are treated for at least five different purposes: (1) To prevent the formation of scale on the heated surfaces; (2) To prevent encrustation or deposition of the material in the feed lines, preheaters, etc.; (3) To prevent the corrosion of the metal; (4) To prevent foaming of the boiler water; (5) To prevent caustic embrittlement or intergranular cracking of the heated surfaces. It frequently happens that a chemical or mechanical treatment may be used for one of these functions without having any effect whatever on the other objects of the treatment.

The presence of dissolved oxygen in boiler water is responsible for pitting and corrosion and many methods have been proposed for removing this dissolved oxygen. The use of sodium sulphite for this purpose is well known (see "Oxygen removal from boiler water by Sodium Sulphite," by Kobe and Gooding, Industrial & Engineering Chemistry, vol. 27, p. 331–333, 1935). The following reaction takes place when the oxygen is removed: $2Na_2SO_3+O_2\rightarrow 2Na_2SO_4$. In this case the sodium sulphite is readily converted to sodium sulphate by the dissolved oxygen present in the water, but caustic embrittlement is not prevented as the sodium sulphite is converted in its reaction with oxygen.

The use of sulphonic acid salts or waste sulphite liquor products in the treatment of boiler water is also well known (French Patent 619,040, French Patent 581,750) (Protecting steel against intercrystalline attack in aqueous solution, by W. C. Schroeder, A. A. Berk, and R. A. O'Brien, A. S. M. E. Transactions for January 1938). However, the use of lignin sulphonate alone does not offer complete protection against caustic embrittlement.

We have discovered that sulphonated organic material such as sodium lignin sulphonate has the property of inhibiting the oxidation of sodium sulphite in aqueous solution. This is illustrated by the following table:

*Table*

| Composition of boiler water | Per cent oxidation of sulphite after— | | |
|---|---|---|---|
| | 5 hours | 16 hours | 48 hours |
| 1250 ppm [1] NaOH—50 ppm $Na_2SO_3$ | 20.0 | 52.4 | 88.3 |
| 1250 ppm NaOH—50 ppm $Na_2SO_3$—500 ppm Na-lignosulphonate | 8.9 | 19.5 | 33.2 |
| 625 ppm NaOH—25 ppm $Na_2SO_3$ | 23.0 | 55.1 | 86.2 |
| 625 ppm NaOH—25 ppm $Na_2SO_3$—250 ppm Na-lignosulphonate | 10.6 | 20.0 | 30.6 |
| 250 ppm NaOH—10 ppm $Na_2SO_3$ | 20.6 | 53.6 | 85.4 |
| 250 ppm NaOH—10 ppm $Na_2SO_3$—100 ppm Na-lignosulphonate | 9.4 | 20.8 | 35.4 |

[1] Abbreviation for parts by weight per million parts of water.

After considerable experimentation we have found that the addition to normal boiler water of suitable amounts of sodium sulphite and a sulphonated organic material of suitable colloidal characteristics such as lignin sulphonate which has the property of inhibiting the oxidation of sodium sulphite to sodium sulphate, produces un-

expected and effective results not obtainable by the use of either material alone and that such mixture offers complete protection against caustic embrittlement.

A thorough study of the reactions taking place between sodium lignosulphonate and the other constituents in the boiler water such as sodium carbonate, sodium hydroxide, sodium phosphate, sodium chloride, sodium sulphate, etc., indicates that lignin sulphonate releases small quantities of sodium sulphite under such condition and thereby lessens somewhat the dispersibility of the lignin sulphonate. However, for normal boiler operations the amount of sodium sulphite thus released is not sufficient to fully prevent caustic embrittlement. We have discovered that the addition of a predetermined quantity of sodium sulphite and sodium lignin sulphonate to the boiler water effectively prevents caustic embrittlement, as illustrated in the following examples:

*Example 1.*—Standard boiler test water containing 500 P. P. M. of sodium hydroxide, 50 P. P. M. of sodium silicate, to which was added 200 P. P. M. of sodium lignin sulphonate, was placed in a Schroeder test bomb (Association of American Railroads Circular No. D. V. 989, entitled "Intercrystalline Cracks in Locomotive Boilers" by W. C. Schroeder, A. A. Berk and R. A. O'Brien), and the solution maintained at a temperature corresponding to 250 lbs. gauge pressure. The solution was in contact with a piece of highly stressed S. A. E. 1020 boiler plate of ½ inch thickness. After 30 days one plate was cracked through 22% of its thickness, the second plate through 25% of its thickness and the third through 35% of its thickness.

*Example 2.*—A similar test was made using a boiler water containing 500 P. P. M. of sodium hydroxide, 50 P. P. M. of sodium silicate, and 10 P. P. M. of sodium sulphite. The plate was cracked through 100% at the end of the 30-day period. Similar tests with the sodium sulphite increased from 10 up to 200 P. P. M. showed 63% cracking. Thus, apparently no practical amount of sodium sulphite alone is satisfactory.

*Example 3.*—Four similar tests were made using a boiler water containing 500 P. P. M. of sodium hydroxide, 50 P. P. M. of sodium silicate, and 200 P. P. M. of sodium lignin sulphonate, to which 10 P. P. M. of sodium sulphite was added. After 30 days in the test block the steel sample showed no sign of cracking whatever. Similar tests with increased amounts of sodium sulphite also showed complete protection. Since the water used in these tests contained approximately 8 P. P. M. of dissolved oxygen there was enough oxygen present to react with 63 P. P. M. of sodium sulphite to convert it to sodium sulphate. Such oxidation was prevented by the presence of the sulphonate organic matter, such as sodium lignin sulphonate, which inhibited oxidation of sodium sulphite.

*Example 4.*—A similar test was made using a boiler water containing 500 P. P. M. sodium hydroxide, 50 P. P. M. sodium silicate, 500 P. P. M. sodium chloride, and 1500 P. P. M. sodium sulphate. The 1020 steel sample was cracked through 61% of its thickness in 30 days.

*Example 5.*—A similar test was made with the same solution as Example 4 with the addition of 200 P. P. M. of lignin sulphonate. The plate cracked through 58% of its thickness in 30 days.

*Example 6.*—A similar test was made using the same solution as in Example 4 but with the addition of 90 P. P. M. of lignin sulphonate and 10 P. P. M. of sodium sulphite. The plate showed no cracking whatever in 30 days.

We have found that the addition of about 10 to 50 parts by weight of a sulphite such as sodium sulphite, or its equivalent, and 50 to 300 parts by weight of a colloidal sulphonated organic compound selected from the group consisting of lignin sulphonate, and sulphite cellulose liquors, such as sodium lignin sulphonate, per million parts of boiler water is an effective concentration for preventing caustic embrittlement under normal boiler operations. We prefer to regulate the amount present in the boiler water by adding known amounts of the constituents to the feed water or directly to the boiler, taking into consideration the number of times the feed water is concentrated in the boiler, this being determined by means well known to those proficient in the art of boiler water treatment. For example, by means of the chloride ratios, per cent blowndown, etc.

Since the exact nature of the reaction causing embrittlement is not known it cannot be said with certainty how a small quantity of sulphite and lignin sulphonate can stop such reaction. In addition to the lignin sulphonate preventing the oxidation of the sulphite, the sulphite may in turn act to maintain the colloidal dispersion of the lignin sulphonate so that it can form a protective coating for the steel, and thus protect it from the action of the concentrated alkali. Another possibility is that the sulphite, or the lignin sulphonate may affect the nature of the oxide film present on the stressed steel plate and thus prevent the concentrated caustic from attacking the intergranular structure.

While the specific examples have referred to sodium sulphite we do not wish to be limited to sodium alone. The active ingredient is the sulphite ion which may be supplied by adding any suitable compound, such, for example, as alkali or alkaline earth sulphites, or bisulphite or other materials that after addition to hot alkaline boiler water will yield sulphite ions.

We prefer to employ as the sulphonated organic material, sodium lignin sulphonate but other sulphonated compounds such as magnesium or calcium ligninsulphonate or concentrated paper mill waste sulphite liquors may be used.

From the chemical nature of quebracho, cutch and from the claims made by other investigators regarding the protection against caustic embrittlement offered by these materials it might be reasoned that they would react in a similar manner with bisulphite. However, our investigation indicates that quebracho actually accelerated the oxidation of bisulphite in aqueous solution and that cutch has little or no action on the oxidation.

Our invention can be conveniently practiced by first preparing suitable boiler water treating compositions containing the usual caustic alkalinity producing compounds, such as caustic soda, sodium carbonate, and other usual water treating ingredients such as phosphates, etc., and adding thereto our previously described agents for preventing caustic embrittlement, i. e. sodium sulphite, or its equivalent, and sodium lignosulphonate or its equivalent, in suitable proportions so as to give the desired range of concentration as previously described. Such compositions can be prepared in suitable proportions so as to meet the requirements of any given boiler water conditions and the composition can be directly used for treating the boiler water.

It is to be understood that many modifications

and changes of our specific embodiments can be made in practicing our invention and that all such variations are intended to be included within the scope of the appended claims.

We claim:

1. The method of treating boiler water used in steam boilers which comprises adding to the normal feed water containing caustic alkalinity producing compounds a mixture of a sulphite selected from the group consisting of alkali and alkaline earth metal sulphites and a colloidal sulphonated organic compound selected from the group consisting of alkali and alkaline earth lignin sulphonates and sulphite cellulose liquors in sufficient proportions to inhibit caustic embrittlement and thereafter introducing the water in a boiler.

2. The method of preventing caustic embrittlement in a steam boiler which comprises adding to the normal feed water containing caustic alkalinity producing compounds a mixture of a sulphite selected from the group consisting of alkali and alkaline earth metal sulphites and a lignin sulphonate selected from the group consisting of alkali and alkaline earth metal lignin sulphonates in sufficient proportions to inhibit the oxidation of free sulphite during normal operation of said steam boiler and thereafter introducing the water in a boiler.

3. The method of preventing caustic embrittlement in steam boilers which comprises adding to the normal feed water containing caustic alkalinity producing compounds a mixture of sodium sulphite and sodium lignin sulphonate in sufficient proportions to inhibit caustic embrittlement and thereafter introducing the water in a boiler.

4. The method of treating boiler water used in steam boilers which comprises adding to the normal feed water a mixture of a sulphite selected from the group consisting of alkali and alkaline earth metal sulphites and a lignin sulphonate selected from the group consisting of alkali and alkaline earth metal lignin sulphonates in sufficient proportions to prevent caustic embrittlement.

5. A method of treating boiler water used in steam boilers which comprises adding to the normal feed water a mixture of a sulphite selected from the group consisting of alkali and alkaline earth metal sulphites and a lignin sulphonate selected from the group consisting of alkali and alkaline earth metal lignin sulphonates in sufficient proportions to result in a concentration of about 10 to 50 parts by weight of soluble sulphite and about 50 to 300 parts by weight of lignin sulphonate per million parts water in the boiler.

6. The method of treating boiler water for use in a steam boiler which comprises adding to the boiler about 10 to 50 parts by weight of sodium sulphite and about 50 to 300 parts by weight of sodium lignosulphonate per million parts of water to prevent caustic embrittlement during boiler operations.

7. A composition for treating boiler water to prevent caustic embrittlement comprising an inorganic sulphite selected from the group consisting of alkali and alkaline earth metal sulphites, a lignosulphonate selected from the group consisting of alkali and alkaline earth metal lignin sulphonates and a caustic alkalinity producing compound for normal boiler operation in suitable proportions when dissolved in boiler water to yield in solution about 10 to 50 parts by weight of sulphite and about 50 to 300 parts by weight of lignosulphonate per million parts of water.

8. A composition for treating boiler water to prevent caustic embrittlement comprising an inorganic sulphite selected from the group consisting of alkali and alkaline earth metal sulphites and a lignosulphonate selected from the group consisting of alkali and alkaline earth metal lignin sulphonates in suitable proportions to yield in solution 10 to 50 parts by weight of sulphite and 50 to 300 parts by weight of lignosulphonate per million parts of water.

9. A composition for treating boiler water to prevent caustic embrittlement comprising sodium sulphite and a sodium lignosulphonate in suitable proportions to yield in solution 10 to 50 parts by weight of sulphite and 50 to 300 parts by weight of lignosulphonate per million parts of water.

10. A composition for treating boiler water to prevent caustic embrittlement comprising an inorganic sulphite selected from the group consisting of alkali and alkaline earth metal sulphites and a colloidal suphonated organic compound selected from the group consisting of alkali and alkaline earth lignin sulphonates and sulphite cellulose liquors in suitable proportions to yield in solution 10 to 50 parts by weight of sulphite and 50 to 300 parts by weight of a colloidal sulphonated organic compound per million parts of water.

11. A process of inhibiting oxidation of an aqueous solution of sodium sulphite which comprises the step of adding to the solution small amounts of lignin sulphonate selected from the group consisting of alkali and alkaline earth metal lignin sulphonates.

12. A composition comprising sodium sulphite inhibited against oxidation by the presence of lignin sulphonate selected from the group consisting of alkali and alkaline earth metal lignin sulphonates.

13. A composition comprising a sodium sulphite inhibited against oxidation by the presence of a colloidal sulphonated organic compound selected from the group consisting of alkali and alkaline earth lignin sulphonates and sulphite cellulose liquors.

PAUL G. BIRD.
WILSON EVANS.
CARLYLE HARMON.
JÖRGEN RICHTER SALVESEN.