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<p>(21) International Application Number: PCT/EP99/07200</p> <p>(22) International Filing Date: 29 September 1999 (29.09.99)</p> <p>(30) Priority Data:</p> <table border="0"> <tr> <td>9821082.6</td> <td>30 September 1998 (30.09.98)</td> <td>GB</td> </tr> <tr> <td>9828260.1</td> <td>23 December 1998 (23.12.98)</td> <td>GB</td> </tr> </table> <p>(71) Applicant (for all designated States except US): ALBRIGHT & WILSON UK LIMITED [GB/GB]; 210-222 Hagley Road West, Oldbury, West Midlands B68 0NN (GB).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): DAVIS, Keith, Philip [GB/GB]; 3 Holly Close, Kinver, Staffordshire DY7 6BP (GB). DOCHERTY, Gordon, Findlay [GB/GB]; 175 High-bury Road, Kings Heath, Birmingham B14 7QS (GB). WOODWARD, Gary [GB/GB]; 49 Balmoral Court, Chad-desley Road, Kidderminster, Worcestershire DY10 3AH (GB).</p> <p>(74) Agent: SAVIDGE, Roger, Gordon, Madgwick; Albright & Wilson UK Limited, 210-222 Hagley Road West, Oldbury, West Midlands B68 0NN (GB).</p>		9821082.6	30 September 1998 (30.09.98)	GB	9828260.1	23 December 1998 (23.12.98)	GB	<p>(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</p> <p>Published <i>Without international search report and to be republished upon receipt of that report.</i></p>
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<p>(54) Title: WATER TREATMENT</p> <p>(57) Abstract</p> <p>Ring opened ethanolamine bis methylene phosphonates and their N-oxides obtained by prolonged boiling (eg. 2 hours to 4 days) of the commercially available mixture of closed and open phosphonates at high alkalinity (eg. greater than pH12) are more effective than the original mixture at inhibiting scale in system containing high concentration of alkaline earth metal.</p>								

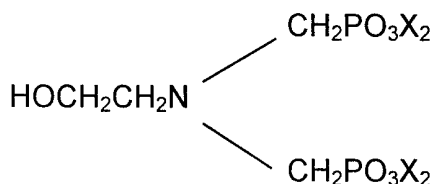
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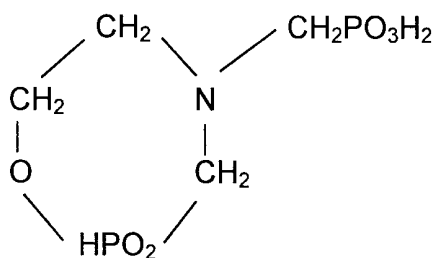
WATER TREATMENT

The invention relates to agents for use in water treatment and in particular to ethanolamine -N, N-bis(methylene phosphonates) having the formula:



where X is hydrogen or a cation such that the resulting salt is water soluble, which will be referred to herein collectively as EBMP, and their N-oxides.

EBMP has been recognised as scale inhibitor which is particularly effective in reducing scale formation in water containing very high levels of calcium and/or barium. It has long been recognised that the method used for commercial manufacture of EBMP, i.e. the reaction of ethanolamine, formaldehyde and phosphorous acid inevitably produces a mixture comprising approximately 50% of EBMP of the formula $\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{PO}_3\text{H}_2)_2$ and 50% of a cyclic ester of EBMP of the formula



While it has been recognised that the cyclic material was less active as a scale inhibitor than EBMP itself, the general view has been summed up in EP O 564 248 page 7 lines 41 to 46 or in GB 2 306 465 page 3 lines 5 to 8.

The former states that since the cyclic ester is itself a scale inhibitor (albeit less active than EBMP itself) it therefore contributes to the overall activity of the composition, and that it is in any case liable to be hydrolysed to EBMP on exposure to alkaline systems under normal conditions of use. The conclusion is expressed that the cyclic material does not therefore constitute a problem.

GB 2 306 465 indicates that the cyclic material positively contributes to the compatibility of commercial EBMP with high concentrations of alkaline earth metals, and that its presence is therefore advantageous.

The N-oxide of EBMP is prepared by reacting the amine with hydrogen peroxide. The use of the N-oxides of such amines in water treatment was described in EP 4 37722. The N-oxide of the cyclic ester was described and stated to be advantageous in US 4 977,292.

Thus the prior art teaches that the presence of the cyclic ester in EBMP is not a problem, but rather an advantage, that it contributes to the scale inhibition properties of the product and is responsible for the property of EBMP which gives rise to its main commercial utility. The N-oxide of the cyclic ester has been specifically claimed as a useful product. It is moreover believed that the cyclic ester is hydrolysed, under normal conditions of use, in alkaline water.

We have now discovered that most of the foregoing assumptions or assertions regarding EBMP and its cyclic ester are false:- The hydrolysis of EBMP cyclic ester requires prolonged heating, e.g. for several hours at reflux in a substantial excess of strong alkali, or for several days at temperatures below reflux, conditions which are not encountered in the normal course of use of the product. We have further discovered that the cyclic ester is substantially ineffective as a scale inhibitor and confers no benefits on the commercial product, either in respect of scale inhibition or compatibility with barium or calcium. Thus prolonged heating of normal commercial EBMP in strong alkali, surprisingly, can almost double its effectiveness.

Our invention therefore, according to one embodiment provides a scale inhibiting composition for addition to aqueous systems which is prepared by heating a mixture of EBMP and its cyclic ester in strongly alkaline aqueous solution and which comprises non-esterified ethanolamine bis(methylene phosphonic acid) or a water soluble salt thereof and less than 50% by weight based on the said non-esterified ethanolamine bis(methylene phosphonic acid) or salt thereof of a cyclic ester of ethanolamine bis(methylene phosphonic acid). Preferably the proportion of cyclic ester is less than 40%, more preferably less than 30%, especially less than 20%, most preferably less than 15%, e.g. less than 10%, ideally less than 5%.

The invention according to a second embodiment provides a method of inhibiting scale formation which comprises adding a scale inhibiting composition as aforesaid to a potentially scale forming aqueous system.

According to a third embodiment the invention provides a method of manufacture of a water treatment agent which comprises the step of heating a composition comprising from 0 to 60% by weight EBMP based on the total weight of the composition and from 40 to 100% by weight of EBMP cyclic ester based on the total weight of the composition with from 3.5 to 10 molar proportions of alkali in aqueous solution at a temperature greater than 100°C for a time sufficient to hydrolyse at least 30% of the weight of said cyclic ester, preferably more than 50%, more preferably more than 60%, especially more than 70%, e.g. from 80% to 95%.

Depending on the temperature and pH the reaction may require from about 4 hours up to 4 days to complete. At reflux temperature we prefer to heat for from 2 to 10 hours, more usually 3 to 8 hours, preferably 3 to 6 hours. The pH should be greater than 10, preferably greater than 11, more preferably greater than 12, most preferably greater than 12.5, especially greater than 13, e.g. 13.5 to 15.

The temperature should preferably be 105 to 150, e.g. 110 to 130°C, and typically reflux temperature, although use of an autoclave to achieve higher temperatures is not excluded. Such higher temperatures may permit the use of shorter heating times.

The reaction mixture preferably has a total solid concentration greater than 20% by weight, more preferably greater than 30% eg. from 40% to saturation.

The product is a highly effective scale inhibitor with particular applications in preventing scaling in oil wells where formation waters contain very high levels of alkaline earth metals and in particular barium, calcium and/or strontium. For example such water usually contains more than 200mg per litre of alkaline earth metal, often more than 500mg per litre and sometimes more than 1000mg per litre. Concentrations above 2000 mg per litre are not unknown.

The great majority of scale inhibitors are ineffective to prevent or significantly inhibit scale under such conditions. EBMP however is highly effective in such systems. The pH of such systems is generally between 4.5 and 9, usually 5 to 8, e.g. 6 to 7.5. Under these conditions there is no tendency for the cyclic component of EBMP to hydrolyse.

The product may be added in concentrations of from 5 to 1000ppm, preferably 10 to 800ppm, more preferably 20 to 700ppm, especially 30 to 600ppm, e.g. 60 to 500ppm.

According to a fourth embodiment the invention provides an N-oxide of EBMP, comprising less than 50% by weight, based on the weight of EBMP N-oxide of the N-oxide of the cyclic ester.

According to a fifth embodiment the invention provides a method of making an N-oxide of EBMP which comprises reacting hydrogen peroxide with a composition according to said first embodiment or a product of the method of said third embodiment.

The N-oxide is sensitive to the conditions required to hydrolyse the cyclic ester and the reaction with hydrogen peroxide should therefore be effected after hydrolysis.

The reaction may be carried out in the presence of a catalyst such as sodium bicarbonate and/or carbonate.

The preparation of the N-oxide is preferably carried out in a conventional manner by reacting the amine with aqueous hydrogen peroxide. The peroxide may be present in a substantially equimolar amount based on the amine or in a (preferably very small) stoichiometric excess, e.g. in a ratio of from 1:0.9, amine to peroxide, to 1:1.1. The excess of peroxide is preferably less than 0.05% based on the stoichiometric weight.

The process is typically carried out in aqueous solution. Optionally, a non phosphonate sequestrant such as EDTA may be used in the preparation which prevents decomposition of the hydrogen peroxide by chelating the metal ions which catalyse its decomposition. Alternative sequestrants include other chelating agents such as pyrophosphate.

The reaction may be performed at elevated temperature, e.g. 20 to 50°C, preferably 30 to 40°C. Higher temperatures, e.g. up to 100°C may be used, but are preferably avoided because of the risk of forming nitrosamines.

The N-oxides are useful as scale and corrosion inhibitors, and as sequestrants. They may be used as cement setting retarders and as deflocculants, e.g. for suspensions of kaolin, calcium carbonate or titanium oxide.

The invention is illustrated by the following examples:-

EXAMPLE 1

EBMP, prepared by reacting together ethanolamine, formaldehyde and phosphorous acid in the presence of hydrochloric acid, contained 50% by weight based on the total solids of cyclic ester.

After boiling for five hours under reflux, at 120°C with 6.5 molar proportions of sodium hydroxide in an aqueous solution containing 50% by weight total solids and having a pH of 14, the composition comprised 94% by weight non-cyclic material based on the total weight of cyclic and non-cyclic.

The cyclic ester separated by crystallisation was compared with the original 50/50 mixture and with the product of the example in a scale inhibition test (tube blocking) using water containing 800mg/l Ca as CaCO₃, 200mg/l magnesium, 800mg/l bicarbonate (as calcium bicarbonate) at pH9, temperature 50° and at a dosage rate of 30ppm by weight of solids. The effectiveness is measured by the drop in pH. The untreated solution gave a final pH of 7.27. The cyclic ester gave a pH of 7.57, which was not a significant difference from the blank. The normal commercial 50/50 mixture gave a final pH of 7.80, the product of the example gave a final pH of 8.57 indicating a substantial improvement.

In conclusion the ring opened material obtained by treatment with strong alkali is highly effective, as a scale inhibitor.

EXAMPLE 2

The product of example 1 is reacted with 1.04 mole % hydrogen peroxide at 40°C. 20% of the total addition of peroxide is first mixed with the EBMP and stirred for 30 minutes until the initial exotherm has subsided and the remainder is added with stirring over 45 minutes and then maintained at 40°C for two hours.

The product is a highly effective sequestrant and scale and corrosion inhibitor.

CLAIMS

1. A scale inhibiting composition for addition to aqueous systems which is prepared by heating a mixture of EBMP and its cyclic ester in strongly alkaline aqueous solution and which comprises non-esterified ethanolamine bis(methylene phosphonic acid) or a water soluble salt thereof and less than 50% by weight based on the said non-esterified ethanolamine bis(methylene phosphonic acid) or salt thereof of a cyclic ester of ethanolamine bis(methylene phosphonic acid).
2. An N-oxide of EBMP, comprising less than 50% by weight, based on the weight of EBMP N-oxide of the N-oxide of the cyclic ester.
3. A composition according to either of Claims 1 and 2 wherein the proportion of cyclic ester is less than 20% by weight based on the weight of EBMP or EBMP N-oxide, respectively.
4. A method of inhibiting scale formation which comprises adding a composition according to either of Claims 1 and 2 to a potentially scale forming aqueous system.
5. A method of manufacture of a water treatment agent which comprises the step of heating a composition comprising from 0 to 60% by weight EBMP based on the total weight of the composition and from 40 to 100% by weight of EBMP cyclic ester based on the total weight of the composition with from 3.5 to 10 molar proportions of alkali in aqueous solution at a pH greater than 10 and at a temperature greater than 100°C for a time sufficient to hydrolyse at least 30% of the weight of said cyclic ester.
6. A method according to claim 5 wherein the heating time is sufficient to hydrolyse more than 70% by weight of said cyclic ester.

7. A method according to claim 5 wherein the temperature is between 110⁰C and 130⁰C
8. A method according to claim 5 wherein the pH is greater than 12.
9. A method according to claim 8 wherein the pH is from 13.5 to 15.
10. A method according to claim 8 or 9 wherein the reaction mixture is refluxed for 2 to 10 hours.
11. A method according claim 4 wherein the composition is added to the aqueous system in a concentration from 5 to 1000ppm.
12. A method of making an N-oxide according to claim 2 which comprises reacting a composition according to claim 1 with hydrogen peroxide.