

SPECIFICATION Water treatment

The present invention relates to water treatment, and in particular to the treatment of scale forming or corrosive water systems, such as the threshold treatment of evaporators, cooling systems or oil wells, in order to inhibit scale formation and/or corrosion.

The evaporation of sea water and other brackish or non-potable waters in order to provide drinking water entails problems of scale deposition on the heat exchange surfaces of the evaporator. It is theoretically possible to prevent scale formation by use of sequestering agents such as phosphates or citrates, capable of forming soluble complexes with the metal ions of the scale forming salts (usually calcium and magnesium ions). However, sequestration of the ions would require the presence of a substantially stoichiometric amount of complexant based on the scale forming ions, which would be prohibitively expensive.

However, there exists a small class of compounds which, when dissolved in water in proportions as low as 0.1 to 100 ppm have the power to inhibit the fouling of heat exchange surfaces by scale. Such concentrations are of a very much smaller order of magnitude than those which would be required to sequester the ions (of the order of several percent by weight). The mechanism of this phenomenon, which is called the threshold effect, is obscure, but it clearly differs from sequestration both because of the very much smaller concentrations of agent required and because many common sequestrants such as citrates do not exhibit threshold properties. Unlike sequestrants, threshold agents may be effective in very small concentrations, even when they do not prevent deposition of solids, by inhibiting the tendency of the deposited solids to form a tenacious scale on the heat exchange surfaces.

Another scaling problem can arise when water is injected in bulk through boreholes into partially exhausted oil bearing strata in order to facilitate the enhanced recovery of residual mineral oil. The water may tend to deposit barium sulphate, barium carbonate, calcium sulphate and/or calcium carbonate scale causing blockage of the boreholes.

Another problem in connection with water treatment is corrosion of metal equipment exposed to water in, for example, cooling water systems. It is known that certain compounds usually in concentrations slightly greater than those required for threshold treatment (e.g. 10 to 500 typically 50 to 200 ppm) tend to inhibit corrosion, especially of iron, steel, copper and their alloys.

It is known that 1-hydroxyethane-1, 1-diphosphonic acid, hereinafter referred to as "HEDP" and its salts exhibit a useful threshold effect, and they have been used successfully to treat evaporators. They are also effective corrosion inhibitors. As used herein, the term HEDP includes homologs of HEDP containing up to 20 carbons e.g. 1-hydroxybutane-1,1-diphosphonic acid or 1-hydroxy-3-phenylpropane-1,1-diphosphonic acid.

We have now discovered that certain dimeric condensates of HEDP exhibit powerful threshold and corrosion inhibiting properties, and are effective at lower dosage rates than HEDP itself and retain effectiveness for longer periods, in certain kinds of water system. They are particularly useful in the treatment of oil wells or water systems which contain traces of strong oxidising agents such as chromate and bromine, which are sometimes present in water systems.

The literature concerning the chemistry of the dimeric condensates of the diphosphonic acids is contradictory. The early work of Prentice, Quimby, Grabenstetter and Nicholson reported in JACS August 1972, pp 6119 to 6124, which formed the basis of a series of Patent Applications, granted or assigned, to Procter and Gamble, indicated that the reaction of a cetic anhydride with phosphorous acid in a non-aqueous solvent could be made to yield a cyclic dimer joined by a P—O—P and a C—O—C bond. The aforesaid workers denied the existence of a dimer containing a C—O—P C—O—P ring. However, subsequent work by Collins, Frazer Perkin and Russell reported in JACS 1974 clearly indicated that the alleged P—O—P, C—O—C cyclic dimer was identical with a product obtained by heating HEDP under vacuum. They presented strong evidence to show that this product is in fact a condensate of the formula:

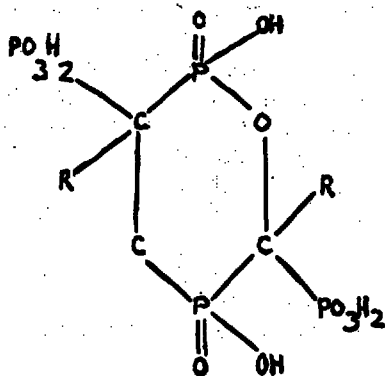


FIGURE 1

; where R is methyl.

The products which we have now found to be of particular value as threshold agents and corrosion inhibitors are dimeric condensates of HEDP which were obtained by heating anhydrous HEDP at 170—180°C under vacuum to remove 1 mole of water per mole of HEDP. The products have been identified as having the formula 1 above where each R is an alkyl, aralkyl or aliphatic ether group having 1 to 20 carbon atoms and will be referred to hereinafter as "HEDP dimer". We believe that the same products may be obtained from the reaction of for example acetic anhydrides with phosphorus acid as described, for example, in B.P. 1,079,340. We have reason to believe that HEDP dimer is also formed as one constituent of the mixture obtained when a tetra metal salt of HEDP is heated as described in B.P. 1,345,518. The term "HEDP dimer" as used herein is not therefore to be construed as limited to HEDP dimer produced by any one particular process, provided that it shall not include the composition prepared by heating the tetra metal salt of HEDP as described and claimed in B.P. 1,345,518. The preferred HEDP dimer is the dimer of 1-hydroxyethane-1,1-diphosphonic acid itself. It will be apparent that the water soluble and sparingly water soluble salts and esters of HEDP dimer are equivalent to the dimer for the purposes of this invention. For convenience, the term "HEDP dimer" will be used herein, where the context so permits, to include such salts and esters.

Our invention accordingly provides a method for the inhibition of scale formation or of corrosion, in aqueous systems which have a tendency or potential to deposit scale or to corrode metal surfaces, which method comprises adding thereto, respectively, a threshold or corrosion inhibiting amount of HEDP dimer as herein defined.

Preferably HEDP dimer is used according to the invention as its alkali metal (e.g. sodium or potassium) or ammonium salts, e.g. its di, tri, or tetra sodium salts or hexammonium salt. Other water soluble salts, including salts of organic bases such as methylamine or trimethylamine are also operative. It is also possible to employ water soluble esters, such as polyoxyethylene esters, or partial esters or their salts, such as the sodium salt of the dimethyl ester. Sparingly soluble derivatives are also operative to give a controlled solubility additive.

The HEDP dimer is preferably used in the proportions conventional in threshold treatment or corrosion inhibition i.e. at concentrations of 0.1 to 100 ppm, preferably 1 to 50 ppm e.g. 2 to 20 ppm for threshold treatment or 5 to 500 ppm, preferably 10 to 200 ppm for corrosion inhibition.

The invention is particularly applicable to the treatment of the sea water which is fed to the evaporators used for making drinking water in ships and arid coastal or island localities, especially chlorinated sea water and most particularly sea water which is subject to continuous chlorination. The HEDP dimer is also of particular use in the treatment of water injected into oil wells during secondary recovery of oil, in order to inhibit the formation of barium or calcium containing scales. The HEDP dimer is most effective in neutral or alkaline solutions.

We have discovered HEDP dimer may be used, according to a further aspect of the present invention in conjunction with other threshold or corrosion inhibiting agents or ingredients of commercial threshold active compositions or corrosion inhibitors such as sodium tripolyphosphate, sodium or potassium hexametaphosphate, HEDP itself, aminomethylene phosphonic acids e.g. amino tris (methylene phosphonic) acid or ethylenediamine tetra (methylenephosphonic) acid; threshold synergists such as dicarboxylic or hydroxycarboxylic acids, e.g. malonic, maleic, malic, tartaric, lactic, citric, adipic, succinic, pimelic, sebacic, or suberic acids; dispersants, e.g. lignin sulphonates, tannin or methylene bis naphthalene sulphonates, polyelectrolytes such as polymaleic acid, polyacrylic acid and polymethacrylic acid; corrosion inhibitors such as water soluble zinc salts, molybdates, nitrites, chromates, silicates, triazoles, substituted thiazoles orthophosphates, polyol esters; biocides, and antifoams. References in the foregoing to acids are to be construed as importing references to the corresponding water soluble or sparingly water soluble salts and esters which are equivalent to the acids for the purposes of this invention. It is within the scope of the present invention that HEDP dimer may also be used in aqueous systems which contain various other inorganic and/or organic materials, particularly all ingredients or substances used by the water treating industry with the proviso that such materials do not render HEDP dimer substantially ineffective for the desired purpose of scale or corrosion inhibition.

According to a further aspect, therefore, our invention provides compositions for threshold treatment which contain from 5 to 95% by weight of the total active material, of HEDP dimer, the balance of the active material consisting essentially of at least one other threshold agent or anti-corrosive agent, and/or at least one dispersant, polyelectrolyte and/or threshold synergist.

By "active material" is meant those ingredients which have threshold anti-corrosive, dispersive, synergistic, or surface activity, and excluding any inert diluent, or any solvent, such as water, which may, optionally be present in the composition.

Threshold synergists are substances, such as maleic or adipic acid which are not in themselves threshold agents, but which enhance the threshold activity of HEDP dimer. Preferably the HEDP dimer is present in a proportion of from 10 to 80% by weight of the total active material, e.g. 30 to 70% most preferably 40 to 60%.

EXAMPLE 1 — THRESHOLD ACTIVITY OF HEDP CYCLIC DIMER

The ability of sub-stoichiometric amounts of HEDP dimer to inhibit the precipitation of calcium carbonate has been demonstrated in a laboratory simulation of an evaporative cooling water system. In this, a naturally hard water from the town supply was recirculated around a system where the flow was alternately heated to about 70°C by a nickel sheathed immersion heater and then cooled to about 40°C in a forced draught cooling column. Scale, formed by the thermal breakdown of calcium bicarbonate, was deposited on the heater sheath and the quantity determined by dissolution methods. A typical analysis of the water used in these experiments was as follows:—

10	Total Hardness	=	149 ppm CaCO ₃	10
	Temporary Hardness	=	78 ppm CaCO ₃	
	Chloride	=	40 ppm Cl	
	pH	=	6.9	

The effectiveness of HEDP Dimer as a threshold agent for calcium carbonate is shown by the following results (Table 1):—

TABLE 1

Inhibitor	Conc ⁿ . ppm.	Scale deposited expressed as mg CaCO ₃	% Inhibition w.r.t. the blank
Blank	0	403	0
HEDP Cyclic Dimer	2	83	79.4

The structure of the dimer was confirmed by the following tests:—

A. ELEMENTAL ANALYSIS**1.1 % Total P.**

20	<u>Breakdown procedure</u>	<u>%P Found</u>	20
	(a) Wet oxidation + persulphate	28.63; 28.65	
	(b) Acid persulphate oxidation	28.66; 28.76	
	(c) Peroxide fusion — Parr bomb	28.75; 28.92	

Mean % Total P = 28.73

1.2 Ortho P; C; H; Moisture

25	<u>Ortho P</u>	<u>50 ppm p</u>	25
	% C	11.9%	
	% C	11.1%	
30	% Moisture (1 hour at 120°C)	12.6%	30

B. MOLECULAR FORMULA

Molecular Formula			Atom Ratio	
%	Found	Theory	Found	Theory
P	28.7	28.84	4.00	4
C	11.1	11.2	4.00	4
H	4.1	4.19	17.7	18
(diff) O	55.3	55.8	14.9	15
H ₂ O	12.6	12.56		

On the results obtained the molecular formula is:—

10 C₄H₁₂P₄O₁₂·3H₂O; Mol. Wt. 430.

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C. STRUCTURAL FORMULA

(i) X-ray

The X-ray powder photograph of the sample was substantially identical with that of the hydrated cyclic dimer prepared by Collins, Frazer, Perkins and Russell (JCS-Dalton, 1974, 960) as:—

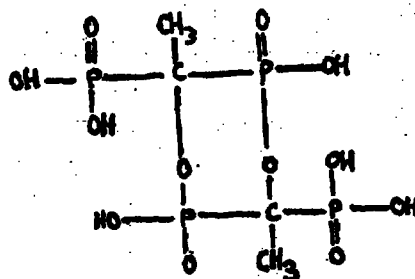
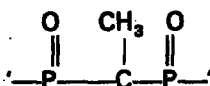


FIGURE 2

(ii) N.M.R.

¹H NMR

The spectrum consists of an 'OH' and a



triplet absorption. The chemical shift of the 'CH₃' is 2 ppmδ and is consistent with this 'CH₃' being in a more strained environment than the corresponding 'CH₃' in HEDP monomer (chemical shift 1.8 ppmδ).

³¹P NMR

The spectrum consists of two complex absorptions of equal intensity, one at -5.2 ppm and the other at -16.0 ppm (from external 85% H₃PO₄ reference), i.e. two magnetically different ³¹P nuclei are present in equal abundance.

By preparing the methyl ester, other works (JACS 1972, 94, 6119) have shown that the -16.0 ppm absorption is due to the 'PO₃' units attached to the ring.

The NMR data given above could be accounted for by either of the following structures:—

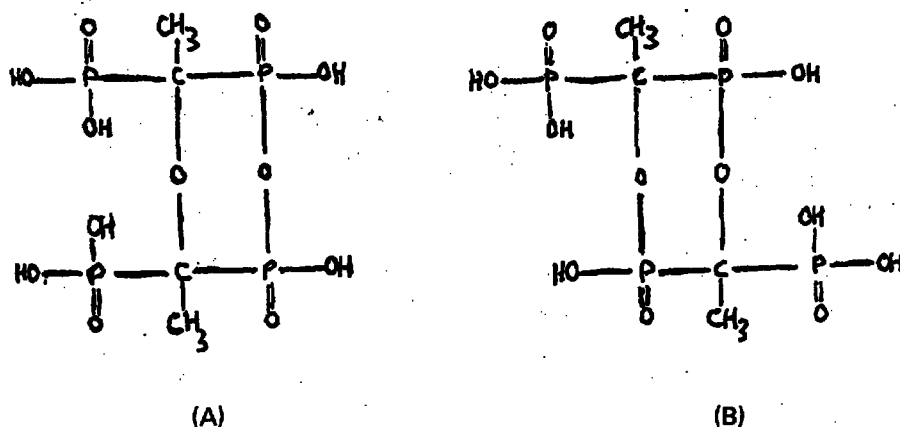


FIGURE 3

Eliminating the proton coupling gave a ^{31}P spectrum consisting of two triplets centred at -5.2 ppm and -16 ppm. This result favours structure B, since structure A should give rise to a more complex spectrum showing both $\text{P}-\text{C}-\text{P}$ and $\text{P}-\text{O}-\text{P}$ coupling, whilst structure B would give $\text{P}-\text{C}-\text{P}$ only.

D. POTENTIOMETRIC TITRATION

Using $0.5-1.0\text{g}$ sample in 100 ml water a potentiometric titration with 1.0N NaOH shows two end-points. The 1st end-point at approximately $\text{pH } 5.5$ corresponds to 4 replaceable H and the second end-point at $\text{pH } 10.7$ to a total of 6 replaceable H .

10 (1) $\text{Br}-\text{NaHCO}_3$

HEDP monomer was added at a level of 10 ppm to a solution containing 100 ppm NaHCO_3 and 10 ppm Br_2 . The resulting solution ($\text{pH } 7.8$) was maintained at 30°C and 20 ml aliquots removed for analysis. The results were as follows:—

Time (Secs)	PO_4 Found (Microgram)	% Decomposition
0	1.9	
90	9.4	4.1
235	14.8	7.0
357	19.9	9.8
533	25.6	12.8
827	31.2	15.8
1200	39.7	20.5
1470	46.0	23.9
1785	54.2	28.3

15 The experiment was repeated using 10 ppm HEDP dimer. Results are as follows.

Time (Secs)	PO_4 Found (Micrograms)	% Decomposition
0	1.1	
320	1.3	0.10
910	1.7	0.30
1845	2.1	0.49

This clearly shows that HEDP dimer is stable. Whereas HEDP monomer is attached under these conditions.

SEA WATER CONTAINING BROMINE — pH 8.3

The cyclic dimer was added to artificial bromine-containing seawater at a level of 10 ppm. The mixture was split into two portions, one of which was allowed to stand at room temperature and the other was heated on a steam bath.

The analytical results are as follows:—

ppm Br ₂ present	Overnight at Room temperature ppm PO ₄ found	Steam bath for 1 hour ppm PO ₄ Found
0	0.31	0.29
2.9	0.32	0.30
6.1	0.35	—
9.0	0.30	0.28
11.0	0.50	0.34
15.1	0.30	0.20

The artificial sea water used in this experiment had the composition.

NaCl	KCl	MgCl ₂ ·6H ₂ O	CaCl ₂ ·6H ₂ O	NaBr	NaHCO ₃	MgSO ₄ ·3H ₂ O	Town Water
265g	7.3g	6.3g	21.7g	2.9g	2.0g	46.9g	to 10 litres
pH adjusted to 8.5							

Compared to results obtained for HEDP monomer in bromine containing water at 30°C. (see example (1).) HEDP dimer shows no evidence for oxidative breakdown in the presence of bromine.

B. ACID AND ALKALINE HYDROLYSIS

(i) 0.5g samples of the dimer hydrate were heated under reflux 4N.H₂SO₄ for 1 hour, (B) 100 ml 4N.H₂SO₄ for 4 hours and (C) 100 ml N.NaOH for 2 hours.

After hydrolysis, each solution was neutralised to pH 8.5 and made up to 200 ml with distilled water.

A 20 ml aliquot was then taken for the determination of HEDP monomer. The results are given in Table 3.

TABLE 3

Hydrolysis Expt.	Dimer Hydrolysed P w/w
BLANK	—
(A) — acid 1 hour	15 ± 1
(B) — acid 4 hour	49 ± 1
(C) — alkali 2 hour	1*

*under the conditions used this result is at the limit of reproducibility of the method.

The results obtained show that the dimer is hydrolysed to monomer in strongly acid solution but is unaffected by N. sodium hydroxide over a similar time scale.

(ii) The possibility of orthophosphate formation by hydrolysis was checked by refluxing 50 mg samples of the dimer for 20 hours with N.NaOH and 9N.H₂SO₄. Each solution was neutralised and made up to 250 ml with distilled water. No orthophosphate (0.5 ppm ortho P) was found in either of these solutions.

The following compositions were prepared and tested by the method of Example 1. All percentages are weight.

EXAMPLE 3

5	6%	HEDP dimer potassium salt	
	14%	Potassium polyacrylate	5
		Balance Water	

EXAMPLE 4

	50%	HEDP dimer	
10	50%	Adipic acid	

EXAMPLE 5

	50%	HEDP dimer	
	50%	Sodium lignin sulphonate	10

EXAMPLE 6

	50%	HEDP dimer	
15	50%	Sodium tripolyphosphate	15

EXAMPLE 7

	80%	HEDP dimer	
	20%	HEDP	

EXAMPLE 8

20	40%	HEDP dimer	20
	60%	Zinc sulphate	

EXAMPLE 9

	75%	HEDP dimer	
25	25%	sodium chromate	

EXAMPLE 10

	60%	HEDP dimer	
	40%	sodium molybdate	25

EXAMPLE 11

	70%	HEDP dimer	
30	30%	sodium nitrite	30

In each case the composition of the example provided satisfactory inhibition of scale formation.

CLAIMS

1. A method for the inhibition of scale formation or of corrosion, in aqueous systems which have a tendency or potential to deposit scale or to corrode metal surfaces, which method comprises adding thereto, respectively, a threshold or corrosion inhibiting amount of HEDP dimer as herein defined.



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2. A method according to claim 1, wherein the water system contains a strong oxidising agent.
3. A method according to claim 2, wherein the strong oxidising agent is bromine.
4. A method according to claim 2, wherein the strong oxidising agent is chromate.
5. A method according to any foregoing claim, wherein HEDP dimer is added as its sodium,
5 potassium and/or ammonium salt. 5
6. A method according to any foregoing claim, wherein HEDP dimer is added in a concentration of from 0.1 to 100 ppm.
7. A method according to any foregoing claim wherein the aqueous system is a sea water evaporator.
10 8. A method according to claim 4, wherein the sea water is subjected to chlorination. 10
9. A method according to any foregoing claim, wherein the aqueous system is neutral or alkaline.
10. A method according to any foregoing claim, substantially as described herein with reference to any of the examples.
11. A threshold treatment or anti-corrosive composition containing from 5 to 95% by weight of
15 the total active material of HEDP dimer as herein defined, the balance of the active material consisting substantially of at least one other threshold treatment and/or anti-corrosive agent, and/or at least one dispersant, and/or at least one threshold synergist and/or at least one biocide and/or anti-foam. 15
12. A composition according to claim 11, wherein the proportion of HEDP dimer is 10 to 80% by weight of the total active material.
20 13. A composition according to claim 12, wherein the proportion of HEDP dimer is 30 to 70% by weight of the total active material. 20
14. A composition according to any of claims 11 to 13, wherein the active material comprises a polyelectrolyte.
15. A composition according to any of claims 11 to 14 wherein the active material comprises a
25 threshold synergist. 25
16. A composition according to claim 15, wherein the threshold synergist is a dicarboxylic acid having from 3 to 10 carbon atoms, or a water soluble or sparingly water salt or ester thereof.
17. A composition according to claim 16, wherein the dicarboxylic acid is adipic acid.
18. A composition according to any of claims 11 to 17 wherein the active material comprises a
30 lignin sulphonate. 30
19. A composition according to any of claims 11 to 18, wherein the active material comprises a condensed phosphate.
20. A composition according to claim 19, wherein the condensed phosphate is an alkali metal tripolyphosphate.
35 21. A composition according to claim 19, wherein the condensed phosphate is an alkali metal hexameta phosphate. 35
22. A composition according to any of claims 11 to 21, wherein the active material comprises HEDP or a water soluble or sparingly water soluble salt or ester thereof.
23. A composition according to any of claims 11 to 22, wherein the active material comprises a
40 zinc salt. 40
24. A composition according to claims 11 to 23 wherein the active material comprises a chromate.
25. A composition according to any of claims 11 to 24 wherein, the active material comprises a molybdate.
45 26. A composition according to any of claims 11 to 25, wherein the active material comprises a nitrate. 45
27. A composition according to claims 11 to 26, wherein the active material comprises an anti-foam and/or biocide.
28. A method according to any of claims 11 to 27 substantially as described herein with
50 references to any of the examples. 50
29. A method for the treatment of aqueous systems comprising adding thereto a threshold or corrosion inhibiting amount of a composition according to any of claims 11 to 28.