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(54) **N-OXYDE DE N,N-BIS-PHOSPHONOMETHYL
2-(HYDROXY) ETHYLAMINE ETHOXYLE ET
SES SELS SOLUBLES**

(54) **ETHOXYLATED N,N-BIS-PHOSPHONOMETHYL
2-(HYDROXY) ETHYLAMINE N-OXIDES AND
WATER-SOLUBLE SALTS THEREOF**

(57) This invention relates to novel organic phosphonate compounds, and more particularly to ethoxylated N,N-bis-phosphonomethyl 2-(hydroxy) ethylamine N-oxides and their water soluble salts. These novel organic phosphonates are useful as water treatment agents which can be employed for the control of scale and/or corrosion.



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ABSTRACT

This invention relates to novel organic phosphonate compounds, and more particularly to ethoxylated N,N-bis-phosphonomethyl 2-(hydroxy) ethylamine N-oxides
5 and their water soluble salts. These novel organic phosphonates are useful as water treatment agents which can be employed for the control of scale and/or corrosion.

FIELD OF THE INVENTION

This invention relates to organic phosphonate compounds and more particularly the organic phosphonates which can be used as water treatment agents.

5 BACKGROUND OF THE INVENTION

10 Much recent research has concerned development of organic water treatment agents for use in scale or corrosion control. Organic corrosion inhibitors which can reduce reliance on the traditional inorganic inhibitors are particularly sought. Among the organic agents suc-
cessfully employed for water treatment are numerous organic phosphonates. These compounds may generally be employed without detrimentally interfering with other commercial water treatment additives. Phosphonic acid
15 compounds have also been used in other fields for such purposes as flame retardants, plasticizers, lubricants and surfactants.

U.S. Patent No. 3,474,133 discloses that certain organo-phosphono-amine oxide compounds can be prepared by
20 oxidizing organo-phosphono amine with a suitable oxidizing agent. For instance ethanol bis(dihydrogen phosphonomethyl) amine can be reacted with H_2O_2 to yield ethanol bis(dihydrogen phosphonomethyl) amine oxide (i.e. $HOCH_2CH_2N(O)(CH_2PO_3H_2)_2$); and tris(dihydrogen
25 phosphonomethyl) amine can be reacted with H_2O_2 to yield tris(dihydrogen phosphonomethyl) amine oxide (i.e. $ON(CH_2PO_3H_2)_3$). It is disclosed that the organo-phosphono amine oxides have utility in practically all fields of organic chemistry wherein their acidic or salt and/or

amine oxide properties can be utilized; and the various utilities indicated for the compounds in such fields include utility as sequestering or chelating agents, water treating agents, stabilizers for peroxy compounds and corrosion inhibitors. In particular, the acids and water soluble salts of the tris(phosphono lower alkylidene) amine oxides are reported to exhibit the property of being effective sequestering agents for metal ions in alkaline mediums. For example, the penta sodium salt of tris(dihydrogen phosphonomethyl) amine oxide is reported to sequester calcium ions in alkaline media in over a mole per mole basis.

U.S. Patent No. 3,336,221 to Ralston discloses that compounds having a methylphosphonic acid (or alkali metal or ammonium salts thereof) bonded to a nitrogen atom (e.g. pentasodium amino tri(methyl phosphonate) and phosphonomethyl ethanolamines) are threshold active compounds, useful for inhibiting the precipitation of various scale-forming compounds (e.g. calcium carbonate).

U.S. Patent No. 3,214,454 to Blaser et al discloses certain acylation products of phosphorous acid (e.g. hydroxyethylidene diphosphonic acid) and use thereof as complex formers for metal ions (e.g. calcium). Delay of calcite precipitation by the use of substoichiometrical amounts of the compounds is disclosed, as is the comparative effectiveness of certain products in preventing scale formation (e.g. in boilers, tubes, etc.).

While as indicated above, various phosphonates have proved useful for particular water treatment applications, many of them nevertheless have important disadvantages when treating water under certain conditions. For

example, many phosphonates such as tri(methylphosphonic acid) are not chlorine resistant and thus degrade in the presence of free chlorine which is commonly used as a disinfectant or biocide in many aqueous systems. Other
5 phosphonates including tris(phosphono lower alkylidene) amine oxide compounds such as tris(dihydrogen phosphonomethyl) amine oxide are considered very sensitive to calcium hardness and are prone to form calcium phosphonate precipitates. There is thus a continuing need
10 for safe and effective water treating agents which are sufficiently versatile to be used when substantial calcium and/or free chlorine is present in the water to be treated.

SUMMARY OF THE INVENTION

15 Ethoxylated N,N-bis-phosphonomethyl 2-(hydroxy) ethylamine N-oxides and their water soluble salts are disclosed in accordance with this invention. These compounds are particularly useful as water treatment agents which can be employed for the control of scale
20 and/or corrosion.

It is an object of this invention to provide a water treatment agent useful for corrosion and/or scale control.

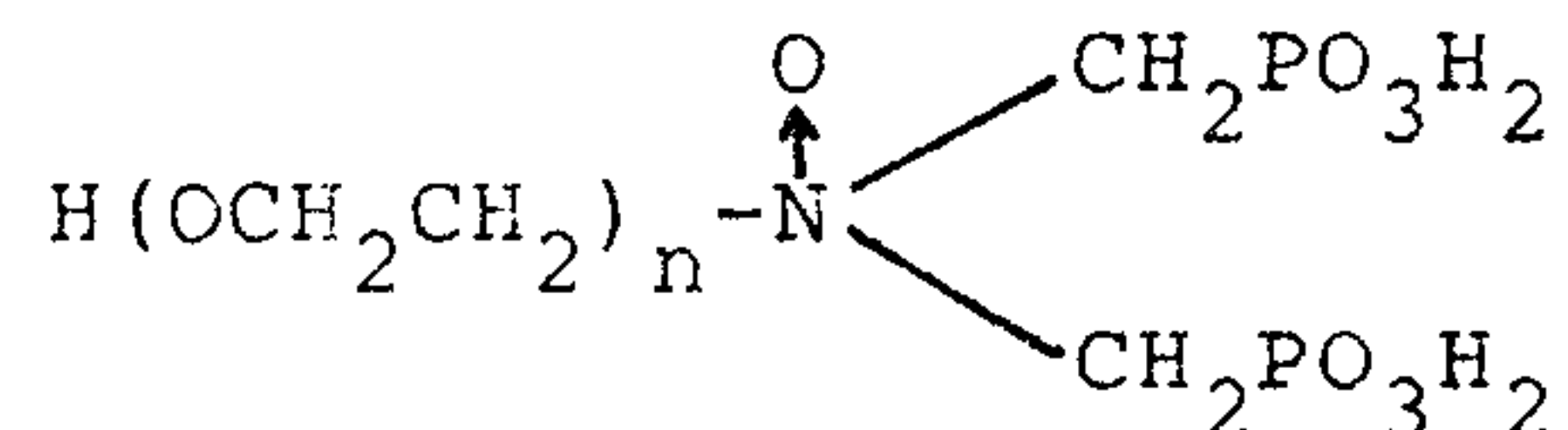
It is another object of this invention to provide a water treatment agent which is considered calcium
25 insensitive.

It is yet another object of this invention to provide a water treatment agent which is resistant to free chlorine in water.

These and other objects and advantages of the present invention will become apparent from the detailed description of the invention which follows.

DETAILED DESCRIPTION OF THE INVENTION

5 This invention relates to the certain ethoxylated N,N-bis-phosphonomethyl 2-(hydroxy)ethylamine N-oxides and their water soluble salts. The ethoxylated N,N-bis-phosphonomethyl 2-(hydroxy)ethylamine N-oxides of this invention include those which may be represented by the
10 general formula



where n is an integer from 2 to 5. The ethoxylated N,N-bis-phosphonomethyl 2-(hydroxy)ethylamine N-oxides (e.g. N,N-bis-phosphonomethyl 2-(hydroxyethoxy)ethylamine N-oxide) may be prepared by conventional oxidation of the trisubstituted nitrogen of the corresponding tertiary phosphonomethyl amine (e.g. N,N-bis-phosphonomethyl 2-(hydroxyethoxy)ethylamine) with a suitable oxidizing agent. Suitable oxidizing agents are generally oxidizing agents which contain an O-O linkage (peroxide compound) and have oxidizing action. Suitable oxidizing agents are considered to include hydrogen peroxide, substituted peroxides and additional compounds of hydrogen peroxide such as the peroxide of sodium and the peroxide of potassium, urea percompounds, percarbonates, perborates, persulfates and the peracids such as persulfuric acid,
25

peracetic acid, peroxyphosphoric acid and the like as well as their water-soluble salt compounds such as sodium, potassium, ammonium and organic amine salts. In general, the oxidation process is usually carried out in an aqueous medium.

Hydrogen peroxide is the preferred oxidizing agent. Reference is made to Hoh et al. "Hydrogen Peroxide Oxidation of Tertiary Amines", The Journal of the American Oil Chemists' Society, Vol. LV, No. 7, pp 268-271 (July 1963) and Lake et al. "Recent Advances in Fatty Amine Oxides. Part I. Chemistry and Preparation", The Journal of the American Oil Chemists' Society, Vol. 40, No. 11, pp. 628-631 (November 1963) for discussion of such oxidations. In general, a solution of the tertiary amine may be advantageously reacted at a pH of about 10 with about 20% excess hydrogen peroxide. It is preferred to use concentrations of hydrogen peroxide above about 2% by weight of the reaction medium.

The water soluble salts are readily prepared from the phosphonomethyl amine oxide by neutralizing the phosphonic acid group with a stoichiometric amount of a base or salt that contains essentially the desired cation or by conversion of the ethoxylated N,N-bis-phosphonomethyl 2-(hydroxy)-ethylamine to a salt form prior to its oxidation to the amine oxide. Bases and salts of acids such as those containing an alkali metal, alkaline earth metal, zinc, aluminum, ammonia and amines are especially suited, with sodium and potassium salts being preferred. For example, to make a sodium salt, a free acid of N,N-bis-phosphonomethyl 2-(hydroxyethoxy)ethylamine N-oxide can be neutralized with a stoichiometric amount of a base containing sodium cation, such as sodium hydroxide.

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Other bases or salts which can be reacted with the free acids to produce salt compounds of the instant invention include the inorganic alkali metal salts, oxides and hydroxides such as Na_2O , Na_2CO_3 , KOH , K_2O , LiOH ,
5 Li_2CO_3 , CsOH , Cs_2CO_3 , other inorganic salts and hydroxides such as $\text{Al}(\text{OH})_3$, $\text{Al}_2(\text{SO}_4)_3$, $\text{Al}(\text{NO}_3)_3$ and ZnSO_4 , and amines, particularly low molecular weight amines (i.e. amines having a molecular weight below about 300), and more particularly the alkyl amines, alkylene amines and
10 alkanol amines containing not more than 2 amine groups such as ethyl amine, diethylamine, propyl amine, propylene diamine, hexylamine, 2-ethyl hexylamine, N-butylethanol amine, triethanolamine and the like.

The tertiary phosphonomethyl amine, N,N-bis-phosphonomethyl 2-(hydroxyethoxy)ethylamine which is useful as a
15 reagent for preparing the preferred compounds of the instant invention can be prepared by the known reaction of a nitrogenous material (i.e. 2-(hydroxyethoxy)ethylamine) with a compound containing a carbonyl group (i.e.
20 formaldehyde) and orthophosphorous acid.

For the foregoing methods of preparation, reaction conditions such as temperatures, pH and time for reaction can be varied with the optimum conditions for the reactions being readily ascertained by those skilled in
25 the art. Reference is made to U. S. Patent No. 3,429,914

for a discussion of the preparation of organo-phosphono amines and organo-phosphono-amine oxides.

The ethoxylated N,N,-bis-phosphonomethyl 2-(hydroxy)ethylamine N-oxides of this invention, especially
30 N,N-bis-phosphonomethyl 2-(hydroxyethoxy)ethylamine N-oxide (i.e. n is 2) and its water soluble salts, are considered useful in water treatment applications. It has

been found that compounds of this invention can be used to inhibit corrosion of metal in aqueous systems as well as to inhibit the formation of scale in such systems. Thus, both the formation of scale and the corrosion of metals can be inhibited in an aqueous system by addition of the compounds of this invention to the system water. Moreover compounds of this invention have been found calcium insensitive and resistant to free chlorine in aqueous solution. In addition metal surfaces can be passivated by the ethoxylated N,N-bis-phosphonomethyl 2-(hydroxy)ethylamine N-oxides. Accordingly the compounds of this invention are considered particularly versatile water treatment agents.

Practice of the invention will become further apparent from the following non-limiting examples.

EXAMPLE I

A solution of 2-(hydroxyethoxy) ethylamine (52.5 grams, 0.5 mole) in water (10 grams) was cooled in an ice-water bath. Phosphorous acid (99%, 82.0 grams, 1 mole) was added slowly to the solution, followed by concentrated hydrochloric acid (37%, 29.6 grams, 0.3 mole). The resultant solution was slowly heated to reflux and formaldehyde (37%, 86.08 grams, 1.07 mole) was added dropwise to the refluxing solution. The solution was allowed to reflux for 13 hours. Analysis of the P^{31} NMR spectra of the product indicates N,N-bis-phosphonomethyl 2-(hydroxyethoxy) ethylamine.

EXAMPLE II

To a solution of N,N-bis-phosphonomethyl 2-(hydroxyethoxy) ethylamine (53.8%, 120.19 grams, 0.2206 mole), sodium hydroxide solution (50%, 82 grams, 1.025 mole) was
5 added dropwise until pH 10.1 was reached. Hydrogen peroxide solution (35.7%, 24.27 grams, 0.255 mole) was added dropwise to the resultant solution. The solution was allowed to stir for 17 hours at ambient temperature. Analysis of the P^{31} NMR spectra of the product indicates
10 N,N-bis-phosphonomethyl 2-(hydroxyethoxy) ethylamine N-oxide.

EXAMPLE III

Calcium sensitivity for the phosphonomethyl amine oxide N,N-bis-phosphonomethyl-2-(hydroxyethoxy) ethylamine
15 N-oxide, was tested using a cloud point test wherein the phosphonomethyl amine oxide was respectively added to a 250-ml beaker containing a hard water solution having a temperature of 60°C, having a pH of 8.3, and containing 500 ppm calcium ion (as $CaCO_3$) and 0.005M borate buffer.
20 Over 100 ppm of N,N-bis-phosphonomethyl-2-(hydroxyethoxy) ethylamine N-oxide, was added without reaching a cloud point (i.e. a point at which the solution becomes turbid). Accordingly the N,N-bis-phosphonomethyl-2-(hydroxyethoxy) ethylamine N-oxide was considered "calcium insensitive".

25 It is noted that not all phosphonates, nor even all organo phosphono amine compounds exhibit the calcium insensitivity of N,N-bis-phosphonomethyl-2-(hydroxyethoxy) ethylamine N-oxide. For example, the addition of about 5 ppm amino tri(methylphosphonic acid) N-oxide or the

addition of about 7 ppm hydroxyethylidene diphosphonic acid each produces a cloud point in the cloud point test described in Example III.

EXAMPLE IV

5 A test solution was formulated to approximate a
4-fold concentrate of Chicago tap water. The water had an
initial pH of about 8.5. Two mild steel coupons were
weighed and suspended for three days in an air-sparged
sample of the solution at 54°C. The steel coupons were
10 then removed and reweighed, and an average corrosion rate
(in mils per year) over the three days was calculated on
the basis of coupon weight loss. The results are provided
in Table A below (Run 1). Three additional runs (Runs 2,
3 and 4) were made using the same procedure except that 15
15 ppm, 30 ppm and 45 ppm N,N-bis-phosphonomethyl-2-(hydroxy-
ethoxy)ethylamine N-oxide were respectively added to the
test solution. The calculated coupon corrosion rates for
these runs are also shown in Table A below.

TABLE A

Run	Additive	Additive Concentration (ppm)	Corrosion Rate (mpy)
	1. None	—	48.0
5	2. N,N-Bis-phosphono- methyl-2-(hydroxye- thoxy) ethylamine N-oxide	15	13.4
10	3. N,N-Bis-phosphono- methyl-2-(hydroxye- thoxy) ethylamine N-oxide	30	3.1
15	4. N,N-Bis-phosphono- methyl-2-(hydroxye- thoxy) ethylamine N-oxide	45	2.9

There was no pH control during the test of this example and the final pH of the test solutions after the three day test ranged from about 8.8 to 9.5.

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EXAMPLE V

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A potentiodynamic polarization test was conducted for demonstrating passivation by a solution of 30 ppm N,N-bis-phosphonomethyl-2-(hydroxyethoxy)ethylamine N-oxide. In this test a disc of 1010 mild steel was polished to 600 grit finished, ultrasonically cleaned in soap water, and rinsed with acetone. The solution was subjected to argon deaeration to achieve an oxygen concentration of less than 0.5 ppm. The solution was adjusted to a pH of 8.5 by using sodium hydroxide or hydrochloric acid and heated to 55°C by a water bath. The disc surface is reduced for 200 seconds at -1 volt against saturated calomel electrode. During the potentiodynamic polarization measurements, the potential is swept at 1 millivolt per second.

The tabularized results for these runs are shown in Table B below.

TABLE B

	Potential (E) (Volts/Saturated Calomel Electrode)	Current Density (I) (Amperes/Square Meter)
5		N,N-Bis-phosphonomethyl -2-(hydroxyethoxy) ethylamine N-oxide (30 ppm)
	-0.850	0.357
	-0.826	0.207
	-0.802	0.042
	-0.778	0.031
10	-0.750	0.103
	-0.726	0.134
	-0.702	0.201
	-0.678	0.234
	-0.654	0.271
15	-0.630	0.286
	-0.602	0.300
	-0.578	0.319
	-0.554	0.325
	-0.546	0.325
20	-0.538	0.326
	-0.530	0.317
	-0.522	0.312
	-0.514	0.303
	-0.506	0.309
25	-0.498	0.288
	-0.490	0.285
	-0.482	0.284
	-0.474	0.276
	-0.466	0.291
30	-0.458	0.295
	-0.450	0.283
	-0.434	0.305
	-0.426	0.321
	-0.418	0.344
35	-0.410	0.347
	-0.402	0.368

An interval of relatively constant current density over a range of potential is considered indicative of passivation. The current density over the potential range of -0.498 to -0.450 is considered indicative of passivation of metal surfaces in the presence of N,N-bis-phosphonomethyl-2-(hydroxyethoxy) ethylamine N-oxide.

EXAMPLE VI

A two ppm solution of N,N-bis-phosphonomethyl-2-(hydroxyethoxy)ethylamine N-oxide in zero hardness water was heated for 24 hours at 60°C. The amount of organic phosphonate which was converted to orthophosphate was then determined. Additional runs (runs 2 and 3) were made using the same solution except that 10 ppm and 20 ppm of NaOCl were respectively added prior to heating. The results are shown in Table C below.

TABLE C

Run	Additive	NaOCl Added (ppm)	% Conversion
1	N,N-Bisphosphonomethyl- -2-(hydroxyethoxy) ethylamine N-oxide	0	0.4
2	N,N-Bisphosphonomethyl -2-(hydroxyethoxy) ethylamine N-oxide	10	4.6
3	N,N-Bisphosphonomethyl -2-(hydroxyethoxy) ethylamine N-oxide	20	5.4

For comparison, N,N-bis-phosphonomethyl ethanolamine and amino tri(methylphosphonic acid) showed 100% and 93% conversion, respectively, under the above testing conditions in the presence of 10 ppm NaOCl. Unlike
5 N,N-bis-phosphonomethyl ethanolamine and amino tri(methylphosphonic acid), the N,N-bis-phosphonomethyl-2-(hydroxyethoxy) ethylamine N-oxide of the instant invention is chlorine resistant.

EXAMPLE VII

10 The ability of the calcium insensitive phosphonomethyl amine oxide, N,N-bis-phosphonomethyl-2-(hydroxyethoxy) ethylamine N-oxide, to also inhibit calcium carbonate formation was demonstrated using a threshold inhibitor test. In this test 800 ml of a test solution
15 containing 400 ppm calcium (as Ca) and 400 ppm bicarbonate (as HCO_3) in a 1000 ml beaker was stirred with a magnetic stir bar and heated using a stainless steel immersion heater to 49°C. The pH was monitored during heating and kept at pH 7.15 with addition of dilute HCl. After the
20 temperature of 49°C was achieved, 0.1 N NaOH was added to the test solution at a rate of 0.32 ml/min using a syringe pump and the rise in pH was monitored. A decrease or plateau in the rate of pH increase is observed when calcium carbonate starts to precipitate, and the pH at
25 which this decrease or plateau is observed is termed the critical pH. The critical pH for the test solution is shown in Table D below along with the total milliequivalents per liter of hydroxide (as NaOH) added to reach the critical pH.

The procedure was repeated using test solution to which 5 ppm of the calcium insensitive N,N-bis-phosphonomethyl-2-(hydroxyethoxy)ethylamine N-oxide was added. A run was also made using amino tri(methylphosphonic acid) N-oxide which as indicated above is considered calcium sensitive when compared to N,N-bis-phosphonomethyl-2-(hydroxyethoxy)ethylamine N-oxide. The results are shown in Table D below.

10

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TABLE D			
Run	Additive	Critical pH	NaOH added to reach critical pH (meq/l)
1	Blank (without treatment)	7.69	0.48
2	N,N-Bis-phosphonomethyl-2-(hydroxyethoxy)ethylamine N-oxide	8.96	2.78
3	Amino tri(methylphosphonic acid) N-oxide	8.50	1.34

As shown in Table D, use of the phosphonomethyl amine oxide of the present invention raised the critical pH and generally resulted in substantially more sodium hydroxide addition before the critical pH was reached. This phosphonomethyl amine oxide is thus an effective threshold inhibitor, capable of inhibiting calcium carbonate precipitation.

EXAMPLE VIII

Scale formation was further tested using an apparatus comprising a covered 28-liter basin, a centrifugal pump which withdraws liquid from the bottom of the basin and

circulates it through tubing respectively to a needle valve which allows flow control, a flow meter which allows flow measurement, a glass housing containing an immersion heater for heating the liquid which is returned to the basin. A cooling coil is provided in the basin and is connected such that tap water may be circulated through the cooling coil. The liquid temperature is controlled using a thermoregulator which activates a solenoid valve which controls the flow of tap water through the coil. A pH probe is also located in the basin and is operably connected to a pH controller which in turn controls a pair of solenoid valves which respectively control flow of 0.5 N NaOH and 0.2 N H_2SO_4 from 1-liter containers to the basin.

Five liters of test solution containing 600 ppm total hardness (as CaCO_3) was transferred to the basin and circulated at a flow rate of 1.4 ft. per second using the centrifugal pump. The pH was controlled within the range of 8.0-8.2 and the variable transformer was turned on such that the heat flux for the immersion heater was 10.9 KBTU per square foot per hour. The cooling coil was operated such that the outlet water from the basin was controlled at 60°C. After six hours the power transformer and the pH controller were turned off and the pH probe was removed from the basin. The water in the basin was cooled rapidly by resetting the thermoregulator to provide tap water circulation through the cooling coil. A sample of test solution was removed from the basin when it had cooled to 35°C, and it was analyzed for total hardness. The results are shown in Table E below. The reduction in total hardness was considered indicative of the scale formation in the system.

10 The run was repeated using the above procedure except
that 2 ppm N,N-bis-phosphonomethyl-2-(hydroxyethoxy)
ethylamine N-oxide was added to the solution prior to
heating. The total hardness of the test solution at the
5 conclusion of these runs are shown in Table E below, as is
the reduction in total hardness, and the calculated
inhibition of scale formation.

TABLE E

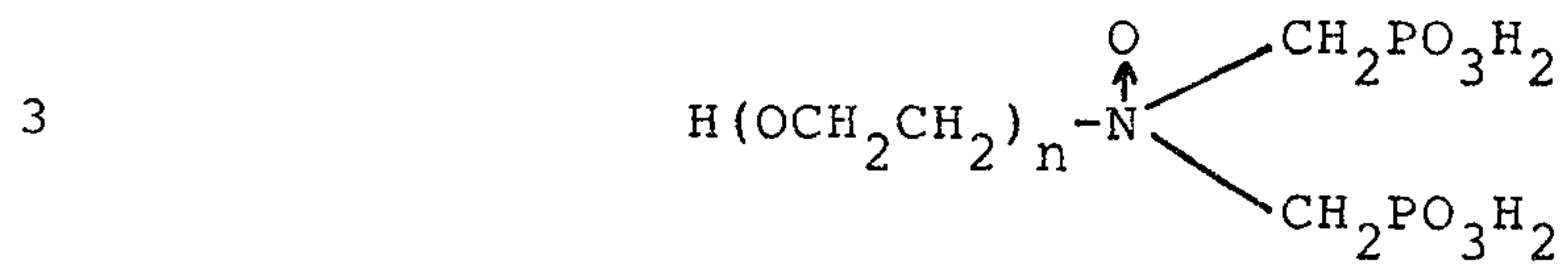
10	Run	Additive	Test Solution Total Hardness (ppm)			Calculated Scale Inhibition %
			Start	End	Change	
	1	Blank (without treatment)	600	134	466	_____
15	2	N,N-Bis-phospho- nomethyl-2-(hydroxy- ethoxy)ethylamine N-oxide (2ppm)	600	580	20	95.7

20 The Examples encompass particular embodiments of the
invention. Other embodiments will become apparent to
those skilled in the art from a consideration of the
specification or practice of the invention disclosed
herein. It is understood that modifications and
variations may be produced without departing from the
25 spirit and scope of the novel concepts of this invention.
It is further understood that the invention is not
confined to the particular formulations and examples
herein illustrated, but it embraces such modified forms
thereof as come within the scope of the following claims.

CLAIMS

WHAT IS CLAIMED IS:

1 1. A compound of the formula



5 where n is an integer from 2 to 5 and water soluble salts thereof.

1 2. A compound according to Claim 1 wherein n is 2.

1 3. A compound according to Claim 1 wherein the
compound is selected from N,N-bis-phosphonomethyl-2-
3 (hydroxyethoxy)ethylamine N-oxide and its sodium and
potassium salts.