ON-STREAM CLEANING COMPOSITIONS AND PROCESS OF USING SAME

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ABSTRACT OF THE DISCLOSURE

Composition for removing iron oxide comprised of (1) a phosphonic acid, either a hydroxyethane phosphonic acid or an aminomethylphosphonic acid, and (2) an aminocetic acid.

This application relates to methods of removing iron oxide and the inhibition of its redeposition from the surfaces, often metal, utilized in aqueous systems. More particularly it relates to the "on-stream" cleaning of such aqueous systems by the use of particular compositions. By the term "on-stream" I mean that the system can be cleaned without either dismantling the system, and without the need to remove it indirectly from service as by changing the nature of the liquid flowing therethrough. In former times it was necessary to shut down the system and to remove or isolate the parts to be cleaned and insert them into a solution of cleaner, or pass a solution of cleaner through the part(s) as by recirculation, under mild heat. While this may have been satisfactory for heat exchangers, these methods have been viewed as being of less desirability than on-stream cleaning due to other disadvantages such processes have associated with them.

One of the largest disadvantages of off-stream cleaning is that large volumes of reagent are required to do a satisfactory job. As a result, often only critical parts were cleaned due to the high cost factor involved. Unfortunately, segments of the total system were still subject to fouling.

The removal of iron oxide deposits, which arise either from the chemical reaction of the water with the metal surfaces of the system's piping and other parts, as well as from being present in certain water supplies, is necessary to inhibit or prevent "under deposit corrosion" of metallic surfaces and for the maintenance of clean heat transfer surfaces.

To explain this further, it is seen that a buildup of metal oxide will affect the rate of heat transfer, will cause the conduits to become clogged and in general add to the corrosive aspect of the water, etc. being used for cooling, heating and other purposes. As is known, a metal surface which is exposed to a corrosive environment, such as water which contains dissolved oxygen and dissolved ionic inorganic solids will be subject to corrosion under the deposits of solids that form on the metal. Thus the term under deposit corrosion. The process of the instant invention inhibits the formation of such corrosion.

In the past, off-stream cleaning and to a degree inhibition of corrosion was accomplished by the use of strong acids such as HCl and sulfamic as well as by the combination of sodium chloride and citric acid. As is self-evident, the handling of these posed certain health dangers. In addition, these reagents, not only removed the undesired substances, but also some amount of base metal. Thus the need for an on-stream cleaning system is easily recognized. Unfortunately prior to now, no such compositions or processes for doing this are known to have existed.

It has now been found that a superior cleaning job can be carried out at less cost without the health hazards of the prior art off-stream cleaning methods, by incorporating my compositions into the aqueous media and cleaning the system during its actual operation.

I have found that a synergistic combination of a phosphonic acid in combination with an amino-methyl carboxylic acid can be utilized to on-stream cleanse aqueous systems.

It is known to the art that phosphonic acids such as sold in the market place under the designation Dequest 2000 by Monsanto, and also that aminomethyl carboxylic acids such as nitritoltriacetic acid, when used alone, each separately, will not remove iron oxide from the metallic surfaces of heat exchangers, boilers, other parts of cooling systems, nuclear reactors, oil wells and the like wherein aqueous system are employed.

I have now found that when the phosphonic acid is used in conjunction with the amino-methyl carboxylic acid that iron oxide will indeed be removed from those surfaces set forth just above, as well as from the metallic surfaces of liquid medium gas separation and purification systems construction of iron, copper, admiralty metal (cupra-nickel alloy) mild steel, stainless steel and brass. Whereas neither works alone at normal use levels of economic concentrations of up to about 10% of either component, my compositions will work effectively at the economic concentrations one is desirous of using.

Accordingly, it is an object of this invention to provide an on-stream cleaning system to remove iron oxide from the surfaces of materials utilized in aqueous systems.

It is another object to provide compositions to be utilized in the on-stream cleaning of aqueous systems.

It is yet another object to provide a method for the on-stream cleaning of the systems employing aqueous media.

It is still another object to provide an on-stream method of inhibiting under deposit corrosion on metal surfaces of aqueous systems, and the compositions to be used therewith.

Other objects will be part obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation and order of one or more of such steps with respect to each of the others and to the compositions possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of which will be indicated in the appended claims.

For a fuller understanding of the nature and objects of the invention, reference should be made to the following detailed description.

The novel compositions of this invention comprise two (2) key ingredients; namely (a) one or more phosphonic acids or their alkaline earth and ammonium derivatives, and (b) one or more amino-methyl carboxylic acids.

Among the phosphonic acids utilizable in this inven-
The above compounds and others in the class can exist in the acid form, or as partially neutralized or totally neutralized salts. None, one or both of the hydroxyl moieties attached to the phosphorus atom can be replaced by the same or different salt forming groups selected from the group consisting of sodium, potassium and ammonium.

Among the amino-methyl carboxylic acids utilizeable herein, mention may be made of ethylenediaminetetraacetic acid, (EDTA); nitrilotriacetic acid (NTA); ammonia diacetic acid also known as iminodiacetic acid (IDA); hydroxy-ethyl-ethylenediaminetetraacetic acid (HEEDTA); diethylene triminediethylene tetraacetic acid (DPTA) and the like.

This combination of ingredients is used in the range of about 1 part amino-methyl carboxylic acid to form 0.1 part to 10.0 parts phosphonic acid, at a use concentration of the combination of ingredients of from 5 to 100 ppm. These compositions will remove from a circulating water system iron oxides such as FeO, FeO\(_2\), Fe\(_3\)O\(_4\) and others if present entirely, i.e. down to the base metal of the metallic parts of the system, with substantially no deleterious effects to the base metal, as by pitting, and/or removal of base metal (general corrosion of a uniform or non-uniform nature).

Not only are my compositions suitable for use in systems constructed entirely of metal, but also in those containing parts of polyvinyl chloride or other similar inert plastics, as in piping. If iron oxide in some way is deposited upon such surfaces, it will be removed, and if not there, no damage will occur from contact with these compositions.

For usage, the compositions of this invention may be premixed with water or other suitable solvent prior to introduction into the system, or both components can be substantially simultaneously introduced into the aqueous system without any prior mixing with a solvent. This will be discussed in more detail supra.

The following non-limiting examples illustrate the preparation of typical compositions for use in aqueous systems, such as cooling systems. Some of these compositions are in the solid particulated state, others of which are in a liquid state. All percentages are by weight, unless otherwise indicated.

**EXAMPLE I**

Fifty parts of the sodium salt of nitrilotri-(methylene phosphonic acid), sold commercially as Dequest 2006 is mixed with 10 parts of nitrilotriacetic acid in forty parts of water. The two particulated components were disposed in the water. Mixing was accomplished by use of a paddle mixer which has a high shearing action, until a uniform paste dispersion was formed, after about thirty minutes of mixing.

**EXAMPLE II**

Forty parts of nitrilotri (methylene phosphonic acid), Dequest 2000, was mixed in the same manner as that employed in Example I, with fifteen parts of the trisodium salt of nitrilotriacetic acid and forty-five parts of water.

**EXAMPLE III**

In like manner fifty parts of the sodium salt of ethane-1-hydroxy-1,1-diphosphonic acid was mixed with fifteen parts of ethylene diamine tetracetic acid and thirty-five parts of water. A paste was prepared.

**EXAMPLE IV**

Eighteen parts of the sodium salt of nitrilotriacetic acid was blended with twenty eight parts of ethane-1-hydroxy-1,1-diphosphonic acid, Dequest 2010 and eighty four parts of water to yield a solution.

**EXAMPLE V**

Twenty five parts of the sodium salt of nitrilotriacetic acid were dry blended with seventy five parts of ethylene diamine tetramethyl phosphonic acid, Dequest 2041, to form a homogeneous powder.

**EXAMPLE VI**

Twenty five parts of the sodium salt of nitrilotriacetic acid were dry blended with seventy five parts of hexamethylene diamine tetramethyl phosphonic acid, Dequest 2051, by a blending operation, as also in Example V, for forty five minutes to yield a composition ready for introduction into the aqueous system.

While not recited in the above examples, a wetting agent such as Aerosol OT or Doufux ZA1 can be mixed into the composition prior to its introduction into the system.

The compositions for use in this invention may be prepared as liquids, powders, pellets, briquettes or other solid forms and introduced into the system by any convenient means as by pumping, slugging, drip feeding and the like to an accessible part of the system by either a continuous feed or intermittent feed method such as to ensure uniform distribution of the cleaning composition throughout the system. The actual point of addition is dependent upon the nature of the system and would be apparent to one skilled in the art.

The composition may be added within the range of from five to about two hundred eighty p.p.m. and preferably in the range of from about twenty to one hundred p.p.m. of composition based on the total liquid volume of the system. If the composition is continuously fed into the system as by a proportioning pump or other metering device, a constant level of the composition should be maintained in the system. If the composition is intermittently added, an average concentration of the desired amount of the composition is maintained in the system.

The decision as to physical form and/or concentration to be utilized, and perhaps to a degree the method of feeding, is influenced by the choice of the two components and whether either or both are soluble or insoluble in aqueous media. Thus in making these decisions it should be borne in mind that among the phosphonic acids, the acid forms of the compounds are solid and water soluble, as are the potassium and ammonium forms, while only certain of the sodium salts are water soluble, the other being of sparing solubility. Whereas with the amino-methyl carboxylic acids, the three salts forms are solids and water soluble, but the acid form of the compounds are substantially insoluble solids. The substantially insoluble components when mixed and added to the aqueous system is soluble in the ranges indicated.

While the range of from five to about two hundred eighty p.p.m. of composition based on the volume of medium has been recited, with five to one hundred being preferred, it is seen that use concentrations as low as one p.p.m. can be employed, though it will take considerably longer time to achieve the desired results. Similarly, a ten percent solution i.e. one hundred thousand p.p.m. of composition can be utilized without damage to the metal.
of the system. However at levels above one hundred p.p.m., the curve of the plotting of time to complete the cleaning versus the concentration utilized, the latter of which is also representative of cost of raw material, indicates an impracticability economically speaking.

The duration of time in the system, the temperature of the system and the concentration of the cleaning composition all affect the reaction kinetics of the cleaning reaction, i.e., the removal of the iron oxides. The compositions of this invention can be utilized at temperatures between the freezing and the boiling points of the aqueous media being utilized or circulated. The pH of the system has substantially no effect on the cleaning process and can accordingly vary from one to fourteen. While factors do affect the kinetics, there is no waiting period of build up time noticed prior to the commencement of the cleaning action once the compositions are added to the aqueous system.

The process of this invention comprises preparing the cleaning composition in a format suitable for and compatible with the aqueous medium of the system, introducing it into the system as by pumping and the like, circulating the medium or letting stand the medium containing the cleaner components for sufficient time, as determined by known methods for the metal oxides to be removed and become complexed in the medium, and removing the cleaner and undesired particles from the system as by replenishment, or filtering of the medium, and disposing of the used medium which contains the undesired materials.

The following non-limiting examples illustrate the process of this invention.

**EXAMPLE VII**

In a petrochemical plant that had had a history of iron oxide fouling in its cooling water system for about two years, the composition for cleaning consisting essentially of thirty parts of Dequest 2006 and twenty parts of NTA acid was fed at the rate of fifty p.p.m. based on the total liquid volume of the system for a period of three months. After this period of time, several of the heat exchangers which had previously been determined to have been heavily coated with iron oxide were now found to be free of iron oxide.

**EXAMPLE VIII**

In a cooling water system of an ammonia plant, iron deposits were prevalent and corrosion rates were determined to be in excess of ten mils per year (m.p.y.). Corrosion was found to be taking place under the deposits of iron oxides. After treating the cooling system with a level of twenty five p.p.m. of the composition of Example VI, for fifty days, the corrosion rate was substantially reduced and determined to be 1.2 m.p.y. The system which prior to introduction into and treatment thereof with a cleaner within the scope of the invention was determined to have a substantial amount of iron oxide therein was now found to be substantially free of iron oxide. It was also found that as a consequence of the treatment-cleaning, that the heat transfer values of the system were sharply improved.

The following examples illustrate the ability of the compounds of the prior art, as well as a typical composition utilizable in this invention to remove iron oxide.

**EXAMPLE IX**

Three hundred milliliter tall beakers were filled with about two hundred ml. of the particular aqueous solution in one containing the cleaner of choice. Coupons which had been rusted by exposure to the atmosphere for sixty days were maintained in the aqueous environment solution at 75°F for twenty four hours. Six solutions of three reagents were utilized. They were, (A) five percent citric acid, (B) five percent inhibited sulfamic acid, (C) five percent of a typical composition utilizable according to this invention and consisting essentially of ninety five percent nitrilotriacetic acid and the sodium salt of Dequest 2006, 4.9%, and a wetting agent 0.5%, this composition being designated T.I.C. (D), (E), and (F) were ten percent solutions of the above.

(A) 5% citric acid:

<table>
<thead>
<tr>
<th>Initial weight</th>
<th>Final weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.8345</td>
<td>9.9490</td>
</tr>
</tbody>
</table>

Weight loss: .9055

Continuous gas evolution during run—iron oxide removed very rapidly. Solution is yellow/green and clear at finish.

(B) 5% sulphamic acid (inhibited):

<table>
<thead>
<tr>
<th>Initial weight</th>
<th>Final weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.8661</td>
<td>10.1250</td>
</tr>
</tbody>
</table>

Weight loss: .7411

Coupon still has light coating of iron oxide at finish, and moderate edge attack. Solution is yellow/amber with slight amount of flaky solid present.

(C) 5% invention composition:

<table>
<thead>
<tr>
<th>Initial weight</th>
<th>Final weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.9255</td>
<td>10.3080</td>
</tr>
</tbody>
</table>

Weight loss: .6175

Solution is slightly cloudy at first; later deep brown with slight granular solid. A soluble iron complex was formed.

(D) 10% citric acid:

<table>
<thead>
<tr>
<th>Initial weight</th>
<th>Final weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.9133</td>
<td>9.4490</td>
</tr>
</tbody>
</table>

Weight loss: 1.4643

Continuous gas evaluation—iron oxide coating is removed within a few minutes. At finish, the solution is yellow/green with a substantial amount of powdery solid present. Increase in total weight loss: 0.5588 g. (61.7%), over 5% solution of (A).

(E) 10% sulphamic acid (inhibited):

<table>
<thead>
<tr>
<th>Initial weight</th>
<th>Final weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.9130</td>
<td>10.0138</td>
</tr>
</tbody>
</table>

Weight loss: .8992

Coupon badly pitted at end. Substantial dark flaky sediment present. Increase in total weight loss: 0.1581 g. (21.3%) over the 5% solution of (B).

(F) 10% invention composition:

<table>
<thead>
<tr>
<th>Initial weight</th>
<th>Final weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.9348</td>
<td>10.2100</td>
</tr>
</tbody>
</table>

Weight loss: .7248

Solution deep brown color. No sediment present. Increase in total weight loss: 0.1013 (16.4%) over the 5% solution.

The above data shows that the increase in weight loss being less for a typical invention composition when the strength is doubled indicates that the inherent corrosiveness of the composition is less for the invention composition than for known prior art cleaners. In addition the sediment remaining from cleaning was substantially less for a typical invention composition.

In order to demonstrate the effectiveness of a typical composition utilizable in this invention, and to contrast it with known prior art compositions which are utilized for off-stream cleaning, as to their ability to remove iron oxide from metal surfaces, and to demonstrate the superiority of my on-stream cleaner, tests were run utilizing a standard distilled water into which had been placed a predetermined amount of a particular cleaner composition.
Each of these water solutions was used in a corrosion test with alcohol cleaned air dried mild steel coupons (A.S.T.M. 1010) in a bath in which the coupons were circulated at a rate to give a water velocity past the coupon of one foot per second. The coupons were one-half (1/2) by two (2) inches by one-sixteenth (1/64) inch. The temperature of the bath was two hundred ten degrees F., for twenty-four hours, at pH 7.0. The corrosion of each coupon is given below in terms of milligrams of weight loss, calculated on a yearly basis. By rotating the coupons which are suspended by an inert holder, in the aqueous medium, the movement of water over metallic surfaces is simulated.

**EXAMPLE X**

| Treatment | M.p.y. 
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphamic acid, 5%</td>
<td>1</td>
</tr>
<tr>
<td>Do</td>
<td>2</td>
</tr>
<tr>
<td>Do</td>
<td>3</td>
</tr>
<tr>
<td>Sulphamic acid, 10%</td>
<td>4</td>
</tr>
<tr>
<td>Do</td>
<td>5</td>
</tr>
<tr>
<td>Sulphamic acid, 15%</td>
<td>6</td>
</tr>
<tr>
<td>Do</td>
<td>7</td>
</tr>
<tr>
<td>NAOH, 25%</td>
<td>8</td>
</tr>
<tr>
<td>Do</td>
<td>9</td>
</tr>
<tr>
<td>Clo2, 25%</td>
<td>10</td>
</tr>
<tr>
<td>Do</td>
<td>11</td>
</tr>
<tr>
<td>Chlorine, 25%</td>
<td>12</td>
</tr>
<tr>
<td>Do</td>
<td>13</td>
</tr>
<tr>
<td>Chlorine, 50%</td>
<td>14</td>
</tr>
<tr>
<td>Do</td>
<td>15</td>
</tr>
<tr>
<td>INH. RGI</td>
<td></td>
</tr>
<tr>
<td>5%</td>
<td>11</td>
</tr>
<tr>
<td>6%</td>
<td>12</td>
</tr>
<tr>
<td>7%</td>
<td>13</td>
</tr>
<tr>
<td>8%</td>
<td>14</td>
</tr>
<tr>
<td>9%</td>
<td>15</td>
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<tr>
<td>10%</td>
<td>16</td>
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<tr>
<td>11%</td>
<td>17</td>
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<tr>
<td>12%</td>
<td>18</td>
</tr>
<tr>
<td>13%</td>
<td>19</td>
</tr>
<tr>
<td>14%</td>
<td>20</td>
</tr>
<tr>
<td>15%</td>
<td>21</td>
</tr>
<tr>
<td>16%</td>
<td>22</td>
</tr>
</tbody>
</table>

1 INH. designates the term Inhibited, said Inhibitor being 0.2% propylic alcohol.
2 The designation T.I.C. is the designation previously assigned to the composition typical of this invention and recited in Example IX.

The above data indicates that the amount of weight loss incurred by the use of T.I.C. is substantially less than that incurred from the use of sulphamic acid, with and without sodium chloride, and substantially less than that incurred from the use of citric acid. The T.I.C. weight losses suffered are on the same order as HCl which has been inhibited. However, and it is a big however, the handling problems associated with the use of HCl do not arise. For instance, no health hazard from the fumes of HCl arises with any of the compositions according to the invention. No disposal problem associated with the use of strong acid is found with exist with my materials. No requirement of low pH of 1 to 2 maintenance which is costly is required. Furthermore there is no heat of solution to be dissipated. T.I.C., as with all of the compositions utilizable according to the invention are used at 6.5 to 7.5 pH, without the requirement of any special handling precautions, and without the creation of any hazards to man or the environment.

The metal oxides which are present and being removed from the system are found adhered to the surfaces of the system components, be they metal, glass, or polyvinyl chloride, in both uniform and non-uniform deposits. These iron oxides which are being removed have arisen from the introduction of iron into the system either from being present in the water being utilized or circulated, or from the oxide of the metal having been removed from surfaces elsewhere in the system by known conventional techniques, downstream.

When oxide particles are removed according to this invention, redissolution is inhibited, as the particles become complexed by the reagents of the compositions and remain substantially uniformly dispersed in the medium as minute discrete particles, which can be flushed away as desired.

Previously, it has been mentioned in brief, that the compositions utilizable in this invention can be introduced as prepared compositions or as the individual components, which when present together act synergistically to accomplish the desired results. It is seen therefore, that the two key components can be introduced in various physical states and various formats, all of which add to the scope of this invention. Thus mention may be made of one liquid-one solid; two liquids; two solids i.e. particulates; as well as liquid admixed with a solid as for instance by encapsulation, or overcoating of a solid by a liquid. Thus the only requirement for any component to be used is that it be soluble in the large volume of medium being utilized. Thus compositions, which are non-aqueous soluble in small amounts of water may be introduced into the aqueous system by solvation in an organic or inorganic liquid compatible with system's aqueous medium.

In summary it is seen that the synergistic combination of ingredients of the compositions of this invention can be utilized according to the process disclosed to cleanse surfaces of iron oxide without the necessity of removing the part from service. That is, the system need not be dismantled for cleaning, i.e. the so-called off-stream cleaning of the prior art. Instead, our compositions are introduced into the system at a convenient point and the cleaning takes place during the actual operation of the particular process, e.g. cooling of engines.

It is readily seen that the prior art off-stream cleaners are not adaptable to our process because of the hazards to men and equipment involved.

It is seen that the process of this invention can be employed in open and closed systems, both warm and cold. The technique can be employed not only in industrial applications, but also in the marine industry. Thus cooling systems of a factory would be treated in like manner as the cooling systems employed on vessels.

Since certain changes may be made in the above compositions and processes without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description should be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A composition for removing iron oxide from a surface, comprising:
   (a) at least one phosphoric acid selected from the group consisting of ethane-1-hydroxy-1, 1-diphosphonic acid, nitritrolith(methylene phosphonic acid), ethylene diamine tetra(methylene phosphonic acid), hexamethylene diamine tetra(methylene phosphonic acid) and the alkalai metal and ammonium derivatives thereof; and
   (b) at least one member selected from the group consisting of ethylene diamine tetracetic acid and a sodium salt thereof, nitritrolith(methylene phosphonic acid) and a sodium salt thereof, iminodiacetic acid, hydroxy ethyl-ethylene diamine triacetic acid, and diethylene triamine pentacetic acid, said components (a) and (b) being present in an amount effective to remove iron oxide from a surface.

2. The composition of claim 1 wherein component (b) is nitritrolith(methylene phosphonic acid).

3. The composition of claim 1 wherein component (b) is a sodium salt of nitritrolith(methylene phosphonic acid).

4. The composition of claim 1 wherein component (b) is ethylene diamine tetraacetic acid.

5. The composition of claim 1 wherein component (b) is a sodium salt of ethylene diamine tetracetic acid.

6. The composition of claim 1 wherein component (a) is ethylene diamine tetra(methylene phosphonic acid).

7. The composition of claim 1 wherein component (a) is ethane-1-hydroxy-1, 1-diphosphonic acid.

8. The composition of claim 1 wherein component (a) is nitritrolith(methylene phosphonic acid) or alkali metal salt thereof.

9. The composition of claim 1 wherein the composition further includes water as a diluent.
10. The composition of claim 2 wherein component (a) is ethane-1-hydroxy-1,1-diphosphonic acid.

11. The composition of claim 2 wherein component (a) is nitritolri(methyleneephosphonic acid) or alkali metal salt thereof.

12. A composition for removing iron oxide from a surface consisting essentially of:
   (a) at least one phosphonic acid selected from the group consisting of ethane-1-hydroxy-1,1-diphosphonic acid, nitritolri(methyleneephosphonic acid), ethylene diamine tetra(methyleneephosphonic acid), hexamethylene diamine tetra(methyleneephosphonic acid) and alkali metal and ammonium derivatives thereof; and
   (b) at least one member selected from the group consisting of ethylene diamine tetraacetic acid and a sodium salt thereof, nitritolriacetic acid, and a sodium salt thereof, iminodiacetic acid, hydroxy-ethyl ethylene diaminetriacetic acid, and diethylene triamine pentacetic acid, said component (a) being present in an amount from about 0.1 part to about 10 parts per one part of component (b).

13. The composition of claim 12 wherein the composition further includes water as a diluent.

14. The composition of claim 12 wherein component (a) is nitritolri(methyleneephosphonic acid) or sodium salt thereof.

15. The composition of claim 14 wherein component (b) is nitritolriacetic acid or sodium salt thereof.

16. The composition of claim 14 wherein component (b) is ethylenediamine tetraacetic acid or sodium salt thereof.

17. The composition of claim 12 wherein component (a) is ethane-1-hydroxy-1,1-diphosphonic acid or sodium salt thereof.

18. The composition of claim 17 wherein component (b) is nitritolriacetic acid or sodium salt thereof.

19. The composition of claim 17 wherein component (b) is ethylenediamine tetraacetic acid or sodium salt thereof.

20. The composition of claim 12 wherein component (a) is ethylene diamine tetra(methyleneephosphonic acid) or sodium salt thereof.

21. The composition of claim 19 wherein component (b) is nitritolriacetic acid or sodium salt thereof.

22. The composition of claim 19 wherein component (b) is ethylenediamine tetraacetic acid or sodium salt thereof.