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# PATENT SPECIFICATION

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## (54) COMPOSITIONS FOR INHIBITING CORROSION AND FORMATION OF SCALE AND SLUDGE IN AQUEOUS SYSTEMS

(71) We, BUCKMAN LABORATORIES INC, a corporation organised and existing under the laws of the State of Tennessee, United States of America, of 1256 North McLean Boulevard, Memphis, Tennessee 38108, United States of America do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to compositions for use in the control of corrosion and of the formation of scale and sludge, such compositions being particularly useful for inhibiting the corrosion of metal parts in contact with aqueous systems and for inhibiting the deposition of scale and sludge on the heat transfer surfaces of cooling water systems and boilers.

It is well known that the operation of commercial and industrial cooling systems is adversely affected by a number of different factors. Of these adverse factors, corrosion of metallic parts in contact with the water is probably one of the most serious. If not controlled, corrosion causes the rapid deterioration of metallic materials used in the construction of cooling towers and associated equipment such as pumps, pipelines and valves, causing major losses in overall efficiency of the cooling systems. While control of bleedoff, pH, and other operating variables is helpful in reducing corrosion, chemical treatment of the water is generally the most effective and economical means of minimizing this problem, particularly where conservation of water by means of recycling is necessary or desired.

Cooling-water systems are also subject to formation of scale deposits. Scaling can occur when the concentration of a dissolved substance in a cooling-water becomes greater than its solubility in the water. It can especially be a problem with a substance that has an inverse solubility curve, that is, a material whose solubility goes down as the temperature goes up. Since water temperatures at or near heat-transfer surfaces are greater than temperatures in the bulk of the system, the solubility of such materials is less in these regions. Consequently, they tend to precipitate and form scales that reduce heat-transfer efficiency.

One principal scale-forming material encountered in cooling-water systems is calcium carbonate formed by the decomposition of calcium bicarbonate. This compound not only has an inverse solubility curve, but its solubility is much lower in most typical cooling-waters than almost all other potential scale-formers that might be present in these waters. Of course, calcium carbonate is soluble in acidic solutions, and as the pH of a cooling water is lowered, scale generally becomes less of a problem. However, most cooling-waters are kept on the alkaline side to reduce corrosion, and thus calcium carbonate scaling remains as a potential problem. Calcium sulfate, calcium phosphate, barium sulfate, and ferric hydroxide can also cause scale. Thus, to be a broadly useful composition, a scale-control product must be capable of controlling different scale types.

Waterside problems encountered in boilers and steam systems include the formation of scale and other deposits, corrosion, and foam. Scale and other deposits on heat-transfer surfaces can cause loss in the thermal efficiency of the boiler and can make the temperature of the boiler metal increase. Under scaling conditions, temperatures may go

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high enough to lead to failure of the metal due to overheating. Corrosion in boilers and steam systems also causes failure of boiler metal and damage to steam and condensate lines.

The principal source of deposits in boilers is dissolved mineral matter in the boiler feedwater. The term "scale" is generally used for deposits that adhere to boiler surfaces exposed to the water, while nonadherent deposits are called "sludge" or "mud". Scale causes more difficulty because the sludge can be purged from the system with the blow-down or can be easily washed out, but scale can normally only be removed by mechanical or chemical cleaning of the boiler.

In natural, untreated water the main sources of scale and sludge are calcium carbonate, calcium sulfate magnesium hydroxide, and silica. The most common type of scale in boilers is probably calcium carbonate, but the most troublesome is usually calcium sulfate. The latter causes more difficulties because its solubility decreases more rapidly with increasing temperatures than does that of other substances, and the scale it forms is hard, dense, and difficult to remove. On the other hand, calcium carbonate tends to form sludge rather than scale, and the calcium carbonate scales that do form are generally softer and easier to remove. Magnesium hydroxide precipitates are not very adherent and tend to form sludges rather than scales.

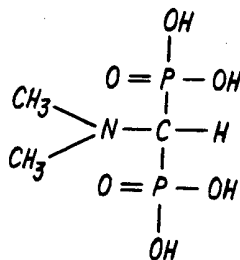
It is one object of this invention to provide stable liquid corrosion-inhibiting and deposit-control compositions, particularly for use in cooling water systems.

According to one feature of the present invention we provide compositions comprising an aqueous medium containing (1) dimethylaminomethylene-bis(phosphonic acid) and/or a water-soluble salt thereof and (2) a water-soluble polymer having a linear hydrocarbon backbone and containing in side chains a carboxylic acid and/or a carboxylic acid salt group, the said polymer having an average molecular weight of from 200 to 100,000.

According to a further feature of the present invention we provide a method of preventing or inhibiting the corrosion or scaling of metal surfaces in contact with an aqueous system which comprises adding to the said system a composition as hereinbefore defined in an amount sufficient to prevent or inhibit such corrosion or scaling.

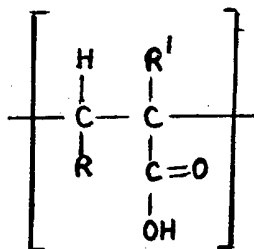
The compositions are preferably employed in the above-described method according to the invention at a concentration of the non-aqueous components thereof of from 0.5 to 1000 ppm in the said aqueous system.

Dimethylaminomethylenebis(phosphonic acid) employed in the composition according to the invention has the following structure:



The two phosphonic acid groups on the molecule provide acidic hydrogens which can be converted to alkali metal, alkaline earth metal and ammonium salts.

The water-soluble polymer having a linear hydrocarbon backbone with side chain carboxylic acid groups may, for example, contain repeating units of the following structure:



(where R represents a hydrogen atom or a -COOH group and R' represents a hydrogen atom or a methyl group) or the corresponding structure wherein one or more of the carboxylic acid groups are in salt form. These polymers may be obtained from

5 acrylic acid or methacrylic acid. Polymers of maleic anhydride can be prepared and the anhydride group hydrolyzed with water to provide carboxylic acid groups. Acrylonitrile and acrylamide polymers may also be hydrolyzed with hot alkaline solutions to eliminate ammonia and form carboxylic acid salts. Copolymers of the above-mentioned monomer containing anhydride, amide, or nitrile groups may also be prepared and these copolymers may be hydrolyzed to form the carboxylic acid groups. These polymers may be utilized as the free acid or as water soluble salts such as the alkali metal and alkaline earth metal salts. The polymers used in this invention are commercially available or may be prepared in conventional manner.

10 The above-defined compositions according to the invention may further advantageously contain phosphorous acid and/or an alkali metal salt thereof, which may, for example, be obtained in anhydrous form or in the form of aqueous solutions containing 50 to 75 percent of the acid.

15 The above-described compositions according to the invention may also advantageously contain one or more water-soluble zinc salts, e.g. zinc acetate, zinc chloride, zinc nitrate or zinc sulfate.

20 The preparation of dimethylaminomethylenebis(phosphonic acid) is described and claimed in our copending Patent Application No. 21014/78 12/2/81. Aqueous solutions of the phosphonic acid or salts of the phosphonic acid can be mixed with solutions of the polymers in water to prepare the compositions of this invention. Phosphorous acid, alkali metal phosphites, and water-soluble zinc salts may then be added if desired, to the aqueous solutions in varying amounts. When zinc salts are used in the compositions of this invention, it may be necessary to decrease the pH of the composition by addition of the appropriate level of phosphorous acid or another mineral acid, e.g. hydrochloric acid, to prevent separation of complex zinc salts.

25 The use of dimethylaminomethylenebis(phosphonic acid) and its alkali metal and ammonium salts for the inhibition of precipitation of insoluble salts from aqueous solutions has been described in U.S. Patent Specification 3,957,160, which suggests that the compound is effective at a molar ratio of  $5 \times 10^{-4}$  to  $5 \times 10^{-2}$  mols per mol of precipitable salt cation. For dimethylaminomethylenebis(phosphonic acid) these values correspond to ratios of 0.27 to 27 parts of the phosphonic acid per 100 parts of calcium.

30 Polyacrylic acid, other carboxylic acid polymers and salts of the polymers are also known to be effective in preventing the precipitation of alkaline earth metal salts and iron salts from aqueous solution.

35 However, neither dimethylaminomethylenebis(phosphonic acid) nor polymeric carboxylic acids are completely satisfactory as water treatment chemicals. The phosphonic acid is most effective in preventing the precipitation of calcium carbonate, but it is much less effective with regard to precipitation of calcium sulfate, calcium acid phosphate, barium sulfate, and ferric hydroxide. The polymeric carboxylic acids are not effective as corrosion inhibitors and the literature does not, to our knowledge, contain any proposals concerning corrosion inhibiting properties of the dimethylaminomethylenebis(phosphonic acid).

40 We have found that the compositions of this invention can be manufactured efficiently and that these compositions provide effective corrosion inhibition of metal parts in contact with aqueous systems. Surprisingly, these compositions are more effective in preventing the precipitation of metal salts from aqueous solutions than would be expected from the combinations of the individual products included in the compositions. This synergism is particularly noted when the compositions are used for scale control at threshold treatment levels.

50 In order to demonstrate the scale inhibiting properties of the compositions of this invention, we have carried out anti-precipitation tests with super-saturated solutions of calcium carbonate, calcium sulfate, calcium acid phosphate, barium sulfate, and ferric hydroxide. The most convenient test methods are related to the demonstration of a "threshold effect," which is defined as a stabilization of super-saturated solutions of scale forming salts by less than stoichiometric concentrations of the anti-precipitants. The mechanism of this effect currently postulates that the anti-precipitant is adsorbed on the growth site of the scalent crystalite during the process of crystallization. This adsorption alters the growth pattern so that the resultant scalent crystals are formed more slowly and are highly distorted. The retardance of crystal growth rate lowers the amount of solid scalent deposited on surfaces. In addition, the distortion of the crystal structure usually gives the scalent solid a different adherence characteristic and the surfaces then have a decreased amount of scale accumulation.

60 This invention is further illustrated by the following Examples and the preparation of dimethylaminomethylenebis(phosphonic acid) is illustrated by Preparations 1 to 6. In these Examples all percentages are on a weight by weight basis.

## Preparation 1.

A reaction flask was charged with 200 grams of bis(2-chloroethyl) ether and 36.5 grams of dimethylformamide and the mixture was treated with 110 grams of phosphorus trichloride added dropwise at such a rate that the reaction temperature was maintained between 20 and 45°C. After one hour agitation at this temperature, the reaction was treated with 63.6 grams of diethylene glycol which was added at such a rate that the reaction temperature did not exceed 45°C. Agitation was continued for two hours at 30 to 45°C after the addition was complete. The reaction was warmed slowly to 70°C and maintained at this temperature for sixteen hours. Twenty grams of water were then added slowly while the temperature was allowed to increase to 95 to 100°C. The mixture was agitated for thirty minutes, after which, an additional charge of 100 grams of water was made. Once again, the reaction was maintained at 95 to 100°C for thirty minutes before being cooled to 60°C and separated in a separatory funnel. The lower aqueous layer was steam distilled to remove bis(2-chloroethyl)ether and treated with acetone to precipitate 72.1 grams (76 percent yield) of dimethylaminomethylenebis(phosphonic acid)monohydrate. The bis(2-chloroethyl)ether removed by steam distillation was combined with the organic layer and a total yield of 283.2 grams (97 percent) was obtained.

## Preparation 2.

A reaction flask was charged with 1200 grams of bis(2-chloroethyl)ether and 220 grams of dimethylformamide and the mixture was treated with 660 grams of phosphorus trichloride added at such a rate that the reaction temperature was maintained between 20 and 45°C. After one hour of agitation at this temperature, the flask was charged with 490 grams of diethylene glycol which was added at such a rate that the temperature did not exceed 45°C. The flask contents were agitated at 20 to 25°C for sixteen hours and then transferred to a glass-lined, steel autoclave. The autoclave was heated at 155 to 165°C for twelve hours and a pressure of 50 pounds per square inch was observed. After cooling and venting, the autoclave contents were treated with 180 grams of water and the temperature was allowed to rise to 90 to 95°C. Agitation at this temperature was continued for thirty minutes and then 1500 grams of additional water were added. The reaction mixture was agitated for eight hours and then separated in a separatory funnel. Analysis of the aqueous layer indicated that a yield of 494.6 grams (94.1 percent) of dimethylaminomethylenebis(phosphonic acid) had been obtained. The yield of bis(2-chloroethyl)ether in excess of that added in the beginning of the reaction was 553.6 grams (83.8 percent).

## Preparation 3.

The procedure of Preparation 1 was followed except that the dimethylaminomethylenebis(phosphonic acid) in the aqueous solution was determined by titration. A yield of 89.3 percent was obtained. The yield of the bis(2-chloroethyl)ether in excess of that used as solvent was 92.1 percent.

## Preparation 4.

The procedure of Preparation 1 was followed except that ethylene dichloride was used in place of bis(2-chloroethyl)ether and ethylene glycol (37.2 grams) was used in place of diethylene glycol. The yield of ethylene dichloride in excess of that used as solvent was 50.8 percent and the yield of dimethylaminomethylenebis(phosphonic acid) was 87.7 percent.

## Preparation 5.

The procedure of Preparation 1 was followed except that ethylene dichloride was used in place of bis(2-chloroethyl)ether and *n*-butyl alcohol (88.8 grams) was used in place of diethylene glycol. The yield of *n*-butyl chloride was 39.2 percent and the yield of dimethylaminomethylenebis(phosphonic acid) was 75.5 percent.

## Preparation 6.

The procedure of Preparation 1 was followed except that *n*-dodecyl chloride was used in place of bis(2-chloroethyl)ether and *n*-dodecyl alcohol (224 grams) was used in place of diethylene glycol. The yield of dodecyl chloride in excess of that used as solvent was 82 percent and the yield of dimethylaminomethylenebis(phosphonic acid) was 56.9 percent.

## EXAMPLE 1.

A composition containing 15 percent of dimethylaminomethylenebis(phosphonic acid) and 15 percent of poly(acrylic acid) in water was prepared by mixing 47.5 grams of an aqueous solution containing 31.6 percent of the trisodium salt of dimethylaminomethylenebis(phosphonic acid), 35.2 grams of an aqueous solution containing 42.6 percent of poly(acrylic acid)(molecular weight—3000), and 17.3 grams of water.

## EXAMPLE 2.

The solution of dimethylaminomethylenebis(phosphonic acid) and Poly(acrylic acid) referred to in Example 1 were used to prepare two formulations. The first contained 17.0 percent each of the phosphonate and polymer and the second solution contained 20.0 percent of the phosphate and 13.0 percent of the polymer. Each of these solutions was then mixed with an aqueous solution containing 70 percent of phosphorus acid to prepare the following compositions:

| Number | Phosphonate | Polymer | Phosphorous acid |
|--------|-------------|---------|------------------|
|        | Percent     | Percent | Percent          |
| 2A     | 16.2        | 16.2    | 3.5              |
| 2B     | 15.3        | 15.3    | 7.0              |
| 2C     | 14.4        | 14.4    | 10.5             |
| 2D     | 19.0        | 12.4    | 3.5              |
| 2E     | 18.0        | 11.7    | 7.0              |
| 2F     | 17.0        | 11.0    | 10.5             |

## EXAMPLE 3.

A composition was prepared using a 31.0 percent solution of the trisodium salt of dimethylaminomethylenebis(phosphonic acid), a 45.6 percent solution of poly(acrylic acid) with a molecular weight of 3300—3500, 70 percent phosphorous acid, 50 percent sodium hydroxide and water to provide the following concentrations:

|                    |              |
|--------------------|--------------|
| Phosphonate        | 16.5 percent |
| Poly(acrylic acid) | 11.0 percent |
| Phosphorous acid   | 6.0 percent  |
| Sodium hydroxide   | 5.5 percent  |

The corrosion inhibiting properties of solutions of this composition with zinc chloride were determined in Example 5.

## EXAMPLE 4.

One hundred grams of a solution containing 20 percent of the trisodium salt of dimethylaminomethylenebis(phosphonic acid) and 13 percent of 3300—3500 molecular weight poly(acrylic acid) were mixed with 15 grams of 37 percent hydrochloric acid and 40 grams of a 50 percent solution of zinc chloride. The corrosion inhibition results using this composition are included in Example 5.

## EXAMPLE 5.

This example illustrates the corrosion-inhibition properties of the compositions. The test apparatus included a sump, a flow circuit, a circulating pump, and a heater. A test fluid was prepared to approximate a moderately hard well water concentrated 4 times which did not come in contact with any metal except for test coupons placed within the circuit in a manner simulating flow, impingement, and sump conditions. The test coupons were 1010 mild steel, and the circulating solution had a calcium hardness as  $\text{CaCO}_3$  of 270 parts per million, a magnesium hardness as  $\text{CaCO}_3$  of 170 parts per million, chloride as  $\text{NaCl}$  of 500 parts per million, and sulfate as  $\text{Na}_2\text{SO}_4$  of 624 parts per million.

The temperature during the test was maintained at about 55°C, and the pH varied from 7 to 9. The test fluid was circulated continuously through the system containing the coupons for a period of seven days. The steel coupons were removed and examined for scale. No significant amount of scale was observed on any of the coupons protected by the compositions of this invention. The coupons were then cleaned and weighed and the corrosion rates calculated as mils per year. One mil per year less is equal to a volume decrease of 0.001 inch per year or 0.0254 millimeter per year. The corrosion rates are included in Table 1.

TABLE 1

Corrosion test results using the compositions of Examples 1, 2, 3, and 4

| Corrosion<br>inhibiting<br>composition | Active<br>ingredient | Zinc*<br>added | Corrosion rate in<br>mils per year |         |             |
|--|----------------------|----------------|------------------------------------|---------|-------------|
|  |                      |                | Example No.                        | Current | Impingement |
|  | Parts per million    |                |                                    |         |             |
| 1                                      | 30                   | —              | 48                                 | 99      | 32          |
| 1                                      | 45                   | —              | 44                                 | 73      | 38          |
| 1                                      | 60                   | —              | 27                                 | 55      | 25          |
| 1                                      | 60                   | 2              | 15                                 | 20      | 16          |
| 1                                      | 60                   | 4              | 10                                 | 18      | 9           |
| 1                                      | 60                   | 6              | 12                                 | 15      | 19          |
| 2A                                     | 36                   | —              | 18                                 | 26      | 20          |
| 2B                                     | 38                   | —              | 15                                 | 18      | 14          |
| 2C                                     | 40                   | —              | 29                                 | 38      | 29          |
| 2D                                     | 35                   | —              | 20                                 | 33      | 31          |
| 2E                                     | 37                   | —              | 10                                 | 15      | 15          |
| 2F                                     | 38                   | —              | 11                                 | 17      | 11          |
| 3                                      | 33.5                 | 3.4            | 11                                 | 23      | 9           |
| 3                                      | 33.5                 | 6.7            | 4                                  | 3       | 4           |
| 3                                      | 33.5                 | 10.1           | 3                                  | 3       | 3           |
| 3                                      | 33.5                 | 13.4           | 2                                  | 3       | 2           |
| 4                                      | 5.4                  | 1.5            | 27                                 | 112     | 41          |
| 4                                      | 10.7                 | 3.1            | 10                                 | 6       | 8           |
| 4                                      | 16.0                 | 4.6            | 9                                  | 24      | 14          |
| 4                                      | 21.3                 | 6.2            | 2                                  | 2       | 1           |
| 4                                      | 31.9                 | 9.3            | 2                                  | 2       | 2           |
| Control                                | —                    | —              | 56                                 | 186     | 44          |

\* The compositions of Example 4 contained zinc in the concentrated formulations.

The results of these tests clearly demonstrate that compositions of this invention have excellent corrosion inhibiting properties when tested against steel coupons in a very aggressive aqueous system.

## EXAMPLE 6.

The composition shown in Table 2 were tested as scale inhibiting preparations in Examples 7—11.

TABLE 2

|   | Trisodium salt of<br>dimethylaminomethylene-<br>bis(phosphonic acid) | Poly(acrylic acid)<br>Mol Wt = 3000—5000 | Phosphoric<br>acid | Phosphorous<br>acid |
|---|--|--|--------------------|---------------------|
|   | Percent<br>(Based on total of active materials)                      | Percent                                  | Percent            | Percent             |
| A | 100  | —  | —                  | —                   |
| B | —  | 100                                      | —                  | —                   |
| C | 75   | 25                                       | —                  | —                   |
| D | 50   | 50                                       | —                  | —                   |
| E | 25   | 75                                       | —                  | —                   |
| F | 61   | 39                                       | —                  | —                   |
| G | 48   | 32                                       | 20                 | —                   |
| H | 43   | 28                                       | 29                 | —                   |
| I | 54   | 36                                       | —                  | 10                  |
| J | 49   | 32                                       | —                  | 19                  |
| K | 72   | 28                                       | —                  | —                   |
| L | 81   | 19                                       | —                  | —                   |
| M | 50   | 32                                       | —                  | 18                  |

- 5 Compositions of this invention included in Table 2 were compared for inhibition of calcium carbonate with the trisodium salt of dimethylaminomethylenebis(phosphonic acid) and poly(acrylic acid). The test was conducted by adding to a bottle 100 milliliters of 0.04 percent solution of calcium hydroxide freshly prepared from recently boiled demineralized water. The compositions being tested were added to provide the calculated concentration desired. Then, 100 milliliters of a 0.05 percent solution of sodium bicarbonate prepared from recently boiled demineralized water was added to the bottle. The final volume was adjusted to 220 milliliters and the solutions were allowed to stand for 18 hours at room temperature. The contents of the bottles were filtered through Whatman No. 4 filter paper (Whatman is a Registered Trade Mark), and the filtered solutions were analyzed for calcium content using an atomic absorption instrument or an EDTA titration procedure. The concentration was 98 parts per million calcium which is equivalent to 245 parts per million of calcium carbonate. The percentage inhibition of precipitation was calculated by dividing the calcium content of the filtrate by 98 and multiplying by 100. The results obtained are included in Table 3.
- 10 20 The results of these tests shown that dimethylaminomethylenebis(phosphonic acid) (A) and poly(acrylic acid) (B) will inhibit the precipitation of calcium carbonate. When the two are combined in various proportions (C, D, E, F), the antiprecipitant properties are maintained and the results with F actually indicate that the overall effectiveness is better than that expected from the combination (synergism). When the phosphonate and poly(acrylic acid) are combined with phosphoric acid (G and H), the antiprecipitant property is greatly decreased. However, combinations with phosphorous acid (I and J) maintain the high level of antiprecipitant effect and the corrosion inhibiting property of
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the composition containing phosphorous acid was demonstrated in Example 5. The startling difference observed with compositions containing phosphoric and phosphorous acids is completely unexpected because of the similarity of the two acids and the relative lack of information in the literature concerning the use of phosphorous acid in water treatment chemical compositions.

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TABLE 3

Results of antiprecipitation tests with calcium carbonate

| Concentration     | Composition        |     |    |    |    |    |    |    |    |    |
|-------------------|--------------------|-----|----|----|----|----|----|----|----|----|
|                   | A                  | B   | C  | D  | E  | F  | G  | H  | I  | J  |
| Parts per million | Percent inhibition |     |    |    |    |    |    |    |    |    |
| 1                 | 16                 | 7   | 10 | 16 | 16 | 18 | —  | —  | 14 | 13 |
| 2                 | 31                 | 25  | 28 | 39 | 36 | 35 | 33 | 27 | 27 | 30 |
| 3                 | 43                 | 91  | 48 | 73 | 61 | 55 | —  | —  | 43 | 45 |
| 4                 | 67                 | 99  | 80 | 84 | 74 | 78 | 47 | 35 | 55 | 61 |
| 5                 | 83                 | 100 | 88 | 89 | 82 | 95 | —  | —  | 70 | 79 |
| 6                 | 98                 | 97  | 85 | 85 | 82 | 98 | 53 | 40 | 90 | 92 |
| 7                 | 94                 | 95  | 85 | 85 | 85 | 99 | —  | —  | 92 | 97 |
| 8                 | 99                 | 97  | 85 | 83 | 88 | 96 | 54 | 42 | 92 | 97 |

## EXAMPLE 8.

The compositions included in Table 2 were tested for inhibition of calcium sulfate scale. This test was conducted by mixing in a bottle 10 milliliters of a solution containing 162.9 grams of calcium chloride per liter of solution (prepared with deionized water) and the desired volume of inhibitor stock solution to provide the desired concentration in a final total volume of 175 milliliters. The pH was then adjusted with dilute HCl or dilute NaOH solutions to 7.0. Twenty-five milliliters of Na<sub>2</sub>SO<sub>4</sub> solution containing 83.45 grams of Na<sub>2</sub>SO<sub>4</sub> per liter of solution was added to the bottle. The final volume was adjusted to 175 milliliters if necessary and the bottle was shaken on a gyratory shaker table at room temperature for 18 hours. Each bottle contained 10,000 parts per million of calcium sulfate.

After shaking, the contents of the bottles were filtered through Whatman No. 4 filter paper and the filtrates were analyzed for calcium content using an atomic absorption spectrophotometer or an EDTA titration procedure. It was necessary to dilute the filtrate before analysis if the calcium content was high. The percentage inhibition of precipitation was calculated by dividing the calcium content of the filtrate by 2940 and multiplying by 100. The results are included in Table 4.

The results included in Table 4 show that the trisodium salt of dimethylamino-methylenebis(phosphonic acid) (A) is not an effective control agent for calcium sulfate. Although poly(acrylic acid) was consistent, it did not inhibit precipitation of calcium sulfate by as much as 70 percent at 10 parts per million. When various combinations of the phosphonic acid and polymer were used (C, D, E, F, K, L), excellent inhibition was obtained in every case. For example, composition D gave 97 percent inhibition of the calcium sulfate at one part per million. All of the combinations were much more effective than would have been expected from the test results with either component, and there is no doubt that synergism was demonstrated in these tests.

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TABLE 4

Results of antiprecipitation tests with calcium sulfate

| Concentration     | Composition        |    |    |    |    |     |     |     |
|-------------------|--------------------|----|----|----|----|-----|-----|-----|
|                   | A                  | B  | C  | D  | E  | F   | K   | L   |
| Parts per million | Percent inhibition |    |    |    |    |     |     |     |
| 1                 | —                  | 62 | —  | 97 | —  | —   | —   | —   |
| 2                 | —                  | 59 | —  | 97 | —  | —   | —   | —   |
| 3                 | —                  | 59 | 97 | 86 | 62 | 93  | 79  | 72  |
| 4                 | —                  | 69 | 97 | 90 | 55 | 90  | 86  | 72  |
| 5                 | 7                  | 69 | 86 | 97 | 62 | 90  | 97  | 83  |
| 6                 | 10                 | 66 | 86 | 90 | 79 | 100 | 100 | 100 |
| 7                 | 7                  | 55 | 90 | 97 | 76 | 100 | 100 | 100 |
| 8                 | 0                  | 66 | 83 | 94 | 90 | 100 | 100 | 100 |
| 9                 | 14                 | 66 | 93 | 94 | 89 | 100 | 100 | 100 |
| 10                | 3                  | 62 | 79 | 97 | 90 | 100 | 100 | 100 |

## EXAMPLE 9.

The compositions included in Table 2 were tested for inhibition of barium sulfate scale. The same procedure as that described in Example 7 was used except that the concentration of barium sulfate present was 255 parts per million. The barium solution used contained 5.35 grams of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  per liter of solution and the sulfate solution contained 1.24 grams of  $\text{Na}_2\text{SO}_4$  per liter of solution. After filtration, the solutions were analyzed for barium using atomic absorption spectrophotometry. The results of the tests are included in Table 5.

The results from the table show that the trisodium salt of dimethylaminomethylene-bis(phosphonic acid) (A) is not a good inhibitor for barium sulfate precipitation but that poly(acrylic acid) is a good inhibitor. Combinations of the two materials (C, D, E, F) shown intermediate effectiveness. However, the outstanding feature of Table 5 is related to the excellent and unexpected results obtained when phosphorous acid is added to the combination of the phosphonic acid and poly(acrylic acid) (M). Composition M gave 75 percent inhibition at a concentration as low as 3 parts per million and 100 percent at 6 parts per million.

TABLE 5

Results of antiprecipitation tests with barium sulfate

| Concentration     | A                  | B   | C  | D  | E  | F   | M   |
|-------------------|--------------------|-----|----|----|----|-----|-----|
| Parts per million | Percent inhibition |     |    |    |    |     |     |
| 3                 | 7                  | 17  | 7  | 0  | 7  | 7   | 75  |
| 6                 | 7                  | 37  | 12 | 33 | 27 | 25  | 100 |
| 9                 | 7                  | 43  | 23 | 30 | 47 | 52  | 100 |
| 12                | 7                  | 70  | 23 | 33 | 57 | 71  | 100 |
| 15                | 7                  | 94  | 77 | 67 | 87 | 80  | 100 |
| 18                | 3                  | 96  | 37 | 33 | 83 | 91  | 100 |
| 21                | 3                  | 100 | 40 | 50 | 77 | 91  | 100 |
| 24                | 3                  | 90  | 57 | 63 | 67 | 88  | 100 |
| 27                | 0                  | 96  | 57 | 67 | 90 | 87  | 100 |
| 30                | 3                  | 96  | 63 | 73 | 87 | 100 | 100 |

Solution M contained 50 percent of trisodium dimethylaminomethylenebisphosphonate, 32 percent of poly(acrylic acid) and 18 percent of phosphorous acid on a 100 percent active basis as described in Table 2.

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## EXAMPLE 10.

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The compositions included in Table 2 were tested for inhibition of calcium acid phosphate precipitation. The same procedure as that described in Example 7 was used except that the concentration of calcium acid phosphate ( $\text{CaHPO}_4$ ) present was 300 parts per million. The calcium solution contained 4.89 grams of  $\text{CaCl}_2$  per liter of solution and the phosphate solution contained 4.70 grams of  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  per liter of solution. The filtered solutions were analyzed by an EDTA titration procedure. The results of these tests are included in Table 6.

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Poly(acrylic acid) (B) is a good inhibitor of  $\text{CaHPO}_4$  but the trisodium salt of dimethylaminomethylenebis(phosphonic acid) is only fair in effectiveness. Combinations of the two materials (C, D, E) provided good inhibition of  $\text{CaHPO}_4$ , at intermediate concentrations and Composition E was even more effective than would be expected from combination of the two materials.

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TABLE 6

Results of antiprecipitation tests with calcium acid phosphate

| Concentration     | Composition        |     |     |     |     |
|-------------------|--------------------|-----|-----|-----|-----|
|                   | A                  | B   | C   | D   | E   |
| Parts per million | Percent inhibition |     |     |     |     |
| 3                 | 0                  | 17  | 0   | 0   | 0   |
| 6                 | 0                  | 13  | 0   | 0   | 0   |
| 9                 | 73                 | 37  | 57  | 17  | 30  |
| 12                | 73                 | 100 | 60  | 80  | 100 |
| 15                | 63                 | 100 | 100 | 77  | 100 |
| 18                | 67                 | 100 | 87  | 77  | 100 |
| 21                | 63                 | 100 | 87  | 83  | 100 |
| 24                | 70                 | 100 | 90  | 100 | 100 |
| 27                | 60                 | 100 | 83  | 100 | 100 |
| 30                | 70                 | 100 | 87  | 100 | 100 |

**EXAMPLE 11.**

5 Inhibition of ferric hydroxide precipitation by compositions included in Table 2  
 was evaluated. A solution containing 14.5 grams of ferric chloride ( $\text{FeCl}_3$ ) per liter of  
 solution was diluted 1 to 50 with deionized water. One hundred milliliters of the dilute  
 solution were mixed with stock solutions of compositions A, B and D. The volume was  
 made to 200 milliliters, and the pH was adjusted to 9.0 with sodium hydroxide solution.  
 The bottles were allowed to stand for 24 hours and were observed for presence of a  
 brown-orange precipitate of ferric hydroxide. Concentrations of 20 parts per million of  
 A and B were required to inhibit precipitation but one 15 parts per million of com-  
 position were required to inhibit precipitation of the ferric hydroxide.

**EXAMPLE 12.**

15 A composition similar to Composition D in Table 2 was prepared by mixing a  
 solution of dimethylaminomethylenebis(phosphonic acid) and a solution of a polymer  
 prepared by polymerizing acrylonitrile and hydrolyzing the polymer with sodium  
 hydroxide to a mixture of sodium polyacrylate and polyacrylamide. The solution was  
 formulated so that approximately equal amounts of the phosphonic acid and polymer  
 were present. This composition was effective as an antiprecipitant and as a corrosion  
 inhibitor.

**EXAMPLE 13.**

20 A composition similar to Composition D in Table 2 was prepared by mixing a  
 solution of dimethylaminomethylenebis(phosphonic acid) and a solution of a polymer  
 prepared by polymerizing maleic anhydride and subsequently hydrolyzing the anhydride  
 group to carboxylic acid groups with sodium hydroxide. The molecular weight of the  
 polymer was in the range of 800 to 2000. The solution was formulated so that approxi-  
 mately equal amounts of the phosphonic acid and polymer were present. This com-  
 position was effective as an antiprecipitant and as a corrosion inhibitor.

**EXAMPLE 14.**

30 A composition was prepared from an aqueous solution of the trisodium salt of  
 dimethylaminomethylenebis(phosphonic acid), an aqueous solution of poly(acrylic acid)  
 having a molecular weight of 4000, and aqueous solution containing 70 percent phos-

phorous acid, an aqueous solution containing 50 percent sodium hydroxide, and water. The concentration present was 17 percent of the trisodium salt of dimethylamino-methylenebis(phosphonic acid), 11 percent of poly(acrylic acid), 6 percent of phosphorous acid, and 5.5 percent of sodium hydroxide. This composition was effective as an antiprecipitant and as a corrosion inhibitor.

#### EXAMPLE 15.

A corrosion and scale inhibition composition was prepared by mixing 100 grams of an aqueous solution containing 20 percent of the trisodium salt of dimethylamino-methylenebis(phosphonic acid) and 13 percent of poly(acrylic acid) having a molecular weight of 3200, 15 grams of 35 percent hydrochloric acid, and 50 grams of an aqueous solution containing 50 percent of zinc chloride.

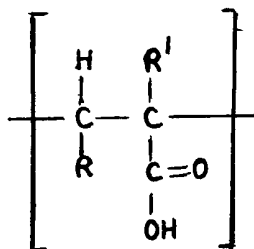
#### EXAMPLE 16.

A corrosion and scale inhibiting composition was prepared by mixing 100 grams of an aqueous solution containing 18 percent of the trisodium salt of dimethylamino-methylenebis(phosphonic acid), 11.7 percent of poly(acrylic acid) having a molecular weight of 3200, and 7 percent of phosphorous acid, 25 grams of 37 percent hydrochloric acid solution, and 50 grams of an aqueous solution containing 50 percent of zinc chloride.

#### WHAT WE CLAIM IS:—

1. Compositions comprising an aqueous medium containing (1) dimethylamino-methylenebis(phosphonic acid) and/or a water-soluble salt thereof and (2) a water-soluble polymer having a linear hydrocarbon backbone and containing in side chains a carboxylic acid and/or a carboxylic acid salt group, the said polymer having an average molecular weight of from 200 to 100,000.

2. Compositions as claimed in claim 1 wherein the said polymer contains repeating units of the following structure



(wherein R represents a hydrogen atom or a —COOH group and R<sup>1</sup> represents a hydrogen atom or a methyl group) or the corresponding structure wherein one or more of the carboxylic acid groups are in salt form.

3. Compositions as claimed in claim 1 wherein the said polymer comprises polyacrylic or polymethacrylic acid or a salt thereof.

4. Compositions as claimed in claim 1 wherein the said polymer comprises hydrolysed poly(maleic anhydride).

5. Compositions as claimed in claim 1 wherein the said polymer comprises hydrolysed polyacrylonitrile.

6. Compositions as claimed in claim 1 wherein the said polymer comprises hydrolysed polyacrylamide.

7. Compositions as claimed in claim 1 wherein the said polymer contains in side chains a carboxylic acid group in the form of an alkali metal or alkaline earth metal salt.

8. Compositions as claimed in any of the preceding claims which further contain phosphorous acid and/or an alkali metal salt thereof.

9. Compositions as claimed in any of the preceding claims which further contain a water-soluble zinc salt.

10. Compositions as claimed in claim 9 wherein the said zinc salt comprises zinc acetate, zinc chloride, zinc nitrate or zinc sulphate.

11. Compositions as claimed in either of claims 9 and 10 further containing hydrochloric acid.

12. Compositions as claimed in claim 1 substantially as herein described.

13. Compositions as claimed in claim 1 substantially as herein described in any of Examples 1 to 16.

14. A method of preventing or inhibiting the corrosion or scaling of metal surfaces in contact with an aqueous system which comprises adding to the said system a composition as claimed in any of the preceding claims in an amount sufficient to prevent or inhibit such corrosion or scaling.

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15. A method as claimed in claim 14 wherein the said composition is employed at a concentration of the non-aqueous components thereof of from 0.5 to 1000 ppm in the said aqueous system.

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