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Description

SCALE CONTROL IN AQUEOUS INDUSTRIAL SYSTEMS

Technical Field

The present invention relates to a composition and method for the chemical treatment of aqueous industrial systems to prevent or reduce the formation of inorganic scales on surfaces within such systems.

Background Art

Contamination of surfaces can be a serious economic problem in many commercial and industrial aqueous processes. This contamination is generally caused by the buildup of organic or inorganic materials on a surface in an aqueous system. Inorganic contaminants in the form of scales are particularly troublesome. Scale formation results from the deposition of mineral compounds present in the water used in an aqueous system. Because they form a hard, rock-like deposit on surfaces in contact with the water, such as the walls of pipes, reservoirs, tanks, and other containment elements in aqueous industrial systems, the formation of scales may cause serious process problems in an aqueous industrial system. Scale formation is especially problematic in geographical areas which have hard water.

Examples of inorganic contaminants which may appear as scales in an aqueous system include barium sulfate, calcium carbonate, calcium sulfate, calcium phosphate, calcium oxalate and other inorganic metal salts which are well known in the art. Often the scale that appears is a mixture of several contaminating materials.

If the formation of scales is not controlled, the buildup of material can interfere with process operations, lower the efficiency of processes, waste

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energy, reduce product quality and result in serious economic disadvantages. For example, aqueous industrial systems such as pulp mills, paper-making machines, oil wells, and the like may encounter problems from inorganic scale buildup. The scale deposits may clog or plug or otherwise reduce the flow of aqueous solutions and/or suspensions in water supply lines, condenser tubes, irrigation lines, and other surfaces associated with aqueous systems.

It is well-known that treating an aqueous system with certain chemical additives can reduce or prevent the formation of inorganic scales on surfaces in an aqueous industrial system. Numerous additives can be used in various situations, depending on the type of scale causing the problem, and also depending on conditions in the industrial system where scale formation occurs. For example, certain organic polymers and copolymers can be added to an aqueous system for this purpose, including polymers and copolymers made from such monomers as acrylic acid, acrylamide, vinyl sulfonic acid, maleic acid, or maleic anhydride; polymers and copolymers made from maleic acid; and terpolymers and copolymers using these and other similar components.

Another group of additives which has been used to reduce or prevent the formation of inorganic scales on surfaces in aqueous systems is polyphosphates. This group may include, but is not limited to, tetrapotassium pyrophosphate, sodium tripolyphosphate, sodium hexametaphosphate, and the like.

Finally, organic compounds that include phosphorus-containing moieties have been used in the battle against inorganic scale buildup. These phosphorous-containing compounds include, but are not limited to, products commonly referred to as

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phosphonic acids, phosphonocarboxylic acids, organic phosphate esters, and the like.

The use of any of the above conventional compounds or additives is well-known to those skilled in the art of scale control in industrial systems.

In many cases, it is possible to achieve enhanced activity against the scaling problem by using various combinations of the compounds and additives listed above, or by using similar compounds and additives and combinations thereof.

For example, it is known that mixtures of polyphosphates with organic polymers similar to and including poly(acrylic acids) are effective in reducing formation of barium sulfate scales. Products containing this combination have been used commercially for many years, and have provided a major benefit by reducing downtime in industrial processes, and improving quality of the product made in these systems.

Although the above additives and combinations have provided various advantages and benefits, it is always advantageous and beneficial to increase the efficacy in reducing or preventing the buildup of scales on surfaces in aqueous systems.

Disclosure of the Invention

Accordingly, the present invention is directed to a composition and method for improving the prevention, reduction, or inhibition of scale buildup on surfaces contacted by an aqueous medium in industrial systems.

A principal advantage of the present invention is the provision of a composition and method for the prevention, reduction, and/or inhibition of barium sulfate scale and/or other types of scale on the surfaces contacted by an aqueous medium in industrial systems where large amounts of water are used.

Additional features and advantages of the invention will be set forth in the description which follows, and in part will be apparent from the description, or may be learned by practice of the invention. The objectives and other advantages of the invention will be realized and attained by the composition and method particularly pointed out in the written description and claims herein as well as in the appended drawings.

To achieve these and other advantages and in accordance with the purpose of the invention, as embodied and broadly described, the present invention is directed to a composition for the prevention, reduction, and/or inhibition of scale buildup in systems utilizing an aqueous medium.

Accordingly, in one aspect of the invention, there is provided a composition having an anionic organic polymer, a polyphosphate compound, and an organophosphonic acid compound, in which the three components are present in an amount effective for controlling the formation of inorganic scales in an aqueous system. Such scales include scales containing barium sulfate, calcium sulfate, calcium carbonate, calcium phosphate, and calcium oxalate.

In another aspect of the invention, there is provided a composition for controlling the formation of scales containing barium sulfate on the surfaces of industrial systems which contact an aqueous medium containing barium sulfate wherein the composition is a mixture having an anionic organic polymer, a polyphosphate compound, and an organophosphonic acid compound. Mixtures having these three components have been found to be very effective in controlling the precipitation or formation of barium sulfate scales.

In a further aspect of the present invention, there is provided a method for controlling the

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formation of inorganic scales on surfaces in contact with an aqueous medium in an aqueous system.

"Contact" as used herein includes periodic or occasional contact as well as continual contact with aqueous systems. The aqueous system is contacted with a composition having an anionic organic polymer, a polyphosphate compound, and an organophosphonic acid compound. These three components are present in a combined amount synergistically effective for controlling the formation of inorganic scales in the aqueous system.

The inventors have found that the addition of an organophosphonic acid to the polyphosphate/organic polymer combinations described above affords a major benefit to increased efficacy in reducing or preventing the buildup of scales on surfaces in aqueous systems.

When the organophosphonic acid compound is used in combination with the polyphosphate compound and the anionic organic polymers in accordance with the present invention, there is a synergistic effect in the prevention, elimination, reduction, and/or inhibition of inorganic scale buildup on the surfaces in contact with aqueous media (including water) which have inorganic scale-building salts therein, in systems and processes which utilize such aqueous media and which are defined herein as aqueous systems or aqueous industrial systems. As shown in the following description and examples, the synergistic effect of the combination of at least one organophosphonic acid compound with at least one anionic organic polymer and at least one polyphosphate compound resulted in a substantial reduction in barium sulfate precipitation from an aqueous medium containing barium sulfate. Accordingly, the composition of the present invention is substantially more effective than the mixtures and

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materials currently known or available for controlling scale buildup. As used herein, controlling the formation of scales, such as barium sulfate scales, is defined as eliminating, preventing, reducing and/or inhibiting the formation of such scales.

The above and other advantages and features of this invention will become apparent upon review of the following detailed description. The accompanying graph is included to provide a further understanding of the invention and is incorporated in and constitutes part of this specification, illustrates several embodiments of the invention and, together with the description, serves to explain the principles of the invention.

Brief Description of the Drawings

Figure 1 is a graphical representation of a cost comparison of barium sulfate scale inhibitors. The cost factor versus percent scale inhibition in aqueous medium having a pH of 5 is shown to illustrate the advantages of the present invention. Over a large range of treatment rates, a combination of polyacrylic acid and polyphosphate gives the result designated by AP. Addition of organic phosphonic acids to this mixture gives the noticeably improved results shown as lines A (for Formula A) and B (for Formula B).

Best Mode for Carrying Out the Invention

In accordance with the present invention, the composition must have at least one of each of an anionic organic polymer, a polyphosphate compound, and an organophosphonic acid compound. These three components of the composition are present in a combined amount effective for controlling the formation of inorganic scales in an aqueous system. According to the invention, the combined amount of an

anionic organic polymer, a polyphosphate compound, and an organophosphonic acid compound achieves superior control of the formation of inorganic scales over the same amount of any of the three components alone or over the same amount of any two of the components combined. Preferably, the compositions of the present invention provide synergistic results in controlling the formation of scales.

The anionic organic polymers (which includes oligomers, homopolymers, copolymers, terpolymers, etc.) used in the composition and method of the present invention include any of the conventional anionic organic polymers used in scale reduction applications. As used herein, anionic organic polymers include, but are not limited to, polymers resulting from the polymerization of one or more of the following monomers: acrylic acid, acrylamide, vinyl sulfonic acid, maleic acid, maleic anhydride, and the like. Examples of such anionic organic polymers include, but are not limited to, polyacrylates, polymaleic acid, polymaleic anhydrides, hydrolyzed polyacrylonitrile, polymethacrylic acid, sulfonated AMPS, vinyl sulfonic acid, and the salts thereof. Other anionic organic polymers that can be used are polymers (preferably copolymers) resulting from the polymerization of one or more of the above-listed monomers with one or more nonionic monomers such as acrylamide, styrene, and the like. The molecular weight of the anionic organic polymers (including copolymers) is not critical and anionic organic polymers used in the present invention may have any molecular weight as well known in the art.

Part of the mechanism of preventing scales from forming is the "dispersing" of the precipitating materials. An anionic polymer will attach to the initial crystal of precipitated material and coat it

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with an anionic charge, thus reducing the likelihood that these crystals will agglomerate and build up on surfaces in contact with aqueous solutions used in aqueous systems, e.g., walls of pipes, reservoirs, and the like. In addition, surfaces generally tend to be anionic so repulsion occurs there as well.

The anionic polymers used in the present invention are generally water-soluble or water-dispersible. Preferably, they are water-soluble.

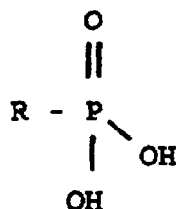
Preferably, the anionic organic polymer in the composition of the present invention is a polyacrylate compound or salts thereof. More preferably, the anionic organic polymer is a polymer of acrylic acid (e.g., a homopolymer of acrylic acid). Most preferably, the anionic organic polymer is a copolymer of acrylic acid and acrylamide having a molecular weight of about 3000 to about 5000. For example, BSI 91, a polyacrylic acid, and BSI 75, a polyacrylic acid copolymer, can be used in the present invention. Both are available from Buckman Laboratories International, Inc. in Memphis, Tennessee.

The polyphosphate compounds used in the composition and method of the present invention include any of the conventional polyphosphate compounds, preferably those used in scale reduction applications. Examples of polyphosphate compounds which may be used in the present invention include, but are not limited to, pyrophosphates and polyphosphates coordinated with sodium or potassium, such as sodium tripolyphosphate, potassium pyrophosphate, and sodium hexametaphosphate. Sodium hexametaphosphate is preferably used at a pH of about 5-6. The preferred polyphosphate compound used in the composition and method of the present invention is a tripolyphosphate. Tripolyphosphates are preferably used at a pH of about 10-11. More preferably, the

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polyphosphate compound used in the present invention is sodium tripolyphosphate.

The organophosphonic acid compounds used in the composition and method of the present invention include any of the conventional phosphorus-containing organic compounds used in water treatment. Any organophosphonic acid compound may be used in accordance with the present invention as long as it produces a synergistic effect in the prevention, elimination, reduction, and/or inhibition of inorganic scale buildup, including barium sulfate scale buildup, on surfaces in contact with aqueous media, when it is combined with an anionic organic polymer and a polyphosphate compound. Preferably, these organic phosphonic acids have the general structure:



Typically, the molecule contains at least several phosphonic acid groups. It may be water-soluble, depending on the characteristics of the R substituent. For example, the R substituent may be an organic amine. Such organophosphonic acids are described in a paper given April 5, 1991 at the Association of Water Technologies in San Antonio, TX by Robert Cavano entitled "Phosphonates: Lore and Legend", the disclosure of which is hereby incorporated by reference.

Examples of organophosphonic acids which may be used in the present invention include, but are not limited to, aminotris (methylenephosphonic acid), diethylenetriaminepenta (methylene phosphonic acid),

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hydroxyethylidenebis (phosphonic acid), tetrakis-methylene phosphonic acid of diaminocyclohexane, tetrakis-methylene phosphonic acid of diamino methyl pentane, the salts of such acids, and the like. Preferably, the organophosphonic acid is selected from aminotris(methylene phosphonic acid), hydroxyethylidenebis (phosphonic acid), tetrakis-methylene phosphonic acid of diaminocyclohexane, and tetrakis-methylene phosphonic acid of diamino methyl pentane.

The amount of organophosphonic acid compound, polyphosphate compound and anionic organic polymer in the composition and method of the present invention is an amount effective to control the formation of inorganic scale buildup on surfaces in contact with aqueous media in systems which utilize aqueous media, i.e., in aqueous systems or aqueous industrial systems, and to provide the synergistic effect discussed herein. Although there is no intention to be limited to specific amounts, in certain aspects of the present invention, the composition has about 0.1% to about 60.0% organophosphonic acid compound; about 1.0% to about 50.0% polyphosphate compound and about 1.0% to about 60.0% anionic organic polymer. In certain preferred embodiments, the composition has about 0.1% to about 10.0% organophosphonic acid compound; about 1.0% to about 20.0% polyphosphate compound and about 1.0% to about 30.0% anionic organic polymer. In the most preferred embodiments, the composition has about 0.1% to about 4.0% organophosphonic acid compound; about 1.0% to about 10.0% polyphosphate compound and about 1.0% to about 20.0% anionic organic polymer. All amounts are given as weight percent based on the total weight of the composition.

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The compositions of the present invention are generally water soluble or water-dispersible and may be added directly to aqueous process streams and/or reservoir and the like as solids, e.g., as free-flowing powders, or they may be dissolved in water at any desired concentrations, e.g., about 25% to about 75% by weight, and added to aqueous process streams, reservoir, and the like in solutions. When the compositions of the present invention are added to an aqueous process stream or a reservoir containing an aqueous medium or to any other aqueous medium in an aqueous system, the composition is in contact with surfaces (e.g., walls of pipes, reservoirs, and the like) in the aqueous system and controls inorganic scale buildup on the surface, i.e., it eliminates, prevents, reduces and/or inhibits the formation of such scales on the surface. The present invention operates both by the presence of the compositions of the invention in aqueous mediums and by the contact of the compositions with surfaces in those mediums as described above.

Other additives may be used in the compositions and method of the present invention as long as they do not have an adverse effect on the control of the formation of scales. For example, conventional water treatment compounds may be used in the composition and method of the present invention. The composition of the present invention may be used at any pH normally encountered in aqueous systems, for example, in oil wells, pulp mills, paper-making processes and the like.

The present invention further relates to a method for controlling the formation of inorganic scales on surfaces in an aqueous system. The aqueous system is contacted with a composition comprising an anionic organic polymer, a polyphosphate, and an

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organophosphonic acid. These three components are present in a combined amount synergistically effective for controlling the formation of inorganic scales in the aqueous system.

The present invention is particularly useful in the reduction or prevention of scales containing barium sulfate. Barium sulfate scales, as well as scales containing other inorganic compounds, may be found in aqueous industrial systems such as paper-making plants, pulp mills, and oil wells.

The composition and method of the present invention is illustrated by way of the following examples. It is to be understood that the invention is not to be limited to the specific conditions or details set forth in these examples except insofar as such limitations are specified in the appended claims.

EXAMPLES

Example 1

The data given below in Table 1 and Table 2 illustrate the synergism provided by the composition of the present invention. At both pH levels 5 and 7, the additive effect from the separate components was much less than the observed result of the combined materials.

First, the following solutions were prepared:

- a 300 ppm solution of barium chloride, prepared by dissolving 0.5336 g of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ per liter of deionized water;
- a 200 ppm sodium sulfate solution, prepared by dissolving 0.2957 g of Na_2SO_4 per liter of deionized water; and
- a 111.11 ppm potassium chloride solution, prepared by dissolving 0.1111 g of KCl per liter of deionized water.

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0.05% active solutions of the composition of the present invention were prepared by making a 0.5% active solution and diluting by a factor of 10.

Formula A contained the ppm dosage of each component below as shown in Table 1. Test results using Formula A are also shown in Table 1.

Formula A: 4.05 parts sodium tripolyphosphate
 4.57 parts polyacrylic acid (X)
 1.38 parts aminotris(methylene
phosphonic
 acid) (A)

Polyacrylic acid X was a copolymer of acrylic acid and acrylamide.

25 ml of the barium chloride solution was mixed with the combination of Formula A in a 2-oz. bottle. The pH of Formula A had been adjusted to be about 10-11 by addition of sodium hydroxide. This is the preferred pH when working with sodium tripolyphosphate. Next, 25 ml of the sodium sulfate solution, its pH adjusted with sodium hydroxide, was introduced. The bottle was capped and allowed to sit overnight at 25°C. Controls were made which contained only 25 ml of the barium solution and 25 ml of the sulfate solution. Blanks were made which contained only 25 ml of the barium solution and 25 ml deionized water.

A 2 ml sample was removed from the bottle and placed with 18 ml of the potassium chloride solution in a centrifuge tube and shaken. The sample was analyzed for barium using an atomic absorption spectrophotometer. Percent inhibition was calculated, based on the ppm of barium in the control subtracted from the ppm of barium in the test sample, divided by the ppm of barium in the control subtracted from the ppm of barium in the blank. This is shown in Tables 1

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and 2 as percent reduction in precipitate.

TABLE 1

Additive Used	Dosage ppm	% Reduction in Precipitate pH 5	% Reduction in Precipitate pH 7
polyphosphate	2.35	11.4	14.7
polyacrylate X	2.65	0.6	0
phosphonic acid A	0.8	0	0
expected result	all above	12.0	14.7
observed result	all above	25.8	21.1

The data in Table 2 are from a variation (Formula B), in which a different commercially available polyacrylate (a homopolymer of acrylic acid) and a different commercially available phosphonic acid were used to prepare the composition of the invention. Formula B, its components listed below, contained the ppm dosage of each component below as shown in Table 2. Test results using Formula B are also shown in Table 2. Again, the combination produced results much better than expected.

Formula B: 4.05 parts sodium tripolyphosphate
 4.57 parts polyacrylic acid (Y)
 1.38 parts
hydroxyethylidenebis(phosphonic
 acid) (B)

TABLE 2

Additive Used	Dosage ppm	% Reduction in Precipitate pH 5	% Reduction in Precipitate pH 7
polyphosphate	2.35	11.4	14.7
polyacrylate Y	2.65	0.2	0
phosphonic acid B	0.8	3.9	0
expected result	all above	15.5	14.7
observed result	all above	25.8	23.7

Figure 1 illustrates in another way the advantage of the present invention. Over a large range of treatment rates, the combination of polyacrylic acid and polyphosphate, an effective commercially available product, gave the result designated by AP. Addition of the organic phosphonic acids to this mixture gave the noticeably improved results shown as lines A (for Formula A) and B (for Formula B). Graph 1 shows the results at pH 5.

Example 2

The present invention was also tested on site in a paper mill. This mill produces in excess of 700 tons per day of linerboard. A recurring problem over

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the years has been buildup of barium sulfate scale in production equipment, including headboxes, and cleaners. This scale can plug holes in the headbox, reducing the quality of the paper produced.

A combination of polyphosphate and polyacrylic acid had been used to reduce problems and increase time between machine shutdowns for required cleanings. At a certain level of treatment, this combination may work very well. Typical treatment in this case is about 0.25 parts per million (ppm) of polyphosphate in the total water flow, and 0.10 ppm polyacrylic acid.

In an attempt to improve performance, a composition according to the present invention, i.e., phosphonic acid, polyphosphate, and polyacrylic acid, was used in the ongoing treatment, replacing the polyphosphate/polyacrylic acid combination. The revised treatment was at a cost equal to that of the original treatment. 25% of the original treatment was replaced by a phosphonic acid. Addition rates were approximately 0.19 ppm polyphosphate, 0.075 ppm polyacrylic acid, and 0.09 ppm phosphonic acid.

As a result of this program, there was a significant reduction in the buildup of barium sulfate scale in this paper machine. After running this program for 6 weeks, all holes in the headbox were clear and unplugged. A small amount of scale that was sighted was extremely light and not problematic. This mill now uses the combination of this invention to control barium sulfate scale.

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Claims

1. A composition comprising:
 - (a) an anionic organic polymer,
 - (b) a polyphosphate,
 - and (c) an organophosphonic acidwherein (a), (b), and (c) are present in a combined amount effective for controlling the formation of inorganic scales in an aqueous system.
2. The composition of claim 1, wherein the anionic organic polymer is a polyacrylate.
3. The composition of claim 2, wherein the polyacrylate is an acrylic acid/acrylamide copolymer.
4. The composition of claim 1, wherein the polyphosphate is sodium tripolyphosphate.
5. The composition of claim 1, wherein the inorganic scales are scales containing inorganic metal salts selected from barium sulfate, calcium carbonate, calcium sulfate, calcium phosphate and calcium oxalate.
6. The composition of claim 5, wherein the inorganic scales are scales containing barium sulfate.
7. The composition of claim 1, wherein the amount of the anionic organic polymer ranges from about 1.0% to about 60.0% by weight; the amount of the polyphosphate ranges from about 1.0% to about 50.0% by weight and the amount of the organophosphonic acid ranges from about 0.1% to about 60.0% by weight.
8. The composition of claim 7, wherein the amount of the anionic organic polymer ranges from about 1.0% to about 30.0% by weight; the amount of the polyphosphate ranges from about 1.0% to about 20.0% by weight and the amount of the organophosphonic acid ranges from about 0.1% to about 10.0% by weight.
9. The composition of claim 8, wherein the amount of the anionic organic polymer ranges from about 1.0% to about 20.0% by weight; the amount of the



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polyphosphate ranges from about 1.0% to about 10.0% by weight and the amount of the organophosphonic acid ranges from about 0.1% to about 4.0% by weight.

10. A method for controlling the formation of inorganic scales on surfaces in an aqueous system, comprising contacting an aqueous system with a composition comprising:

- (a) an anionic organic polymer,
- (b) a polyphosphate,

and (c) an organophosphonic acid

wherein (a), (b), and (c) are present in a combined amount synergistically effective for controlling the formation of inorganic scales in the aqueous system.

11. The method of claim 10, wherein the inorganic scales are scales containing barium sulfate.

12. The method of claim 10, wherein the aqueous system is a paper making machine, a pulp mill, or an oil well.

