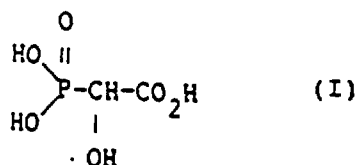


Description

The present invention relates to a process for conditioning metal surfaces to inhibit corrosion of the metal surfaces and/or deposition of scale thereon.

British Patent Application 2,112,370 A describes a method of treating an aqueous system to inhibit corrosion of metals, especially ferrous metals, in contact with the aqueous system and/or to inhibit scale deposition from the aqueous system, the aqueous system containing from 0.1 to 50,000 ppm of 2-hydroxyphosphonoacetic acid having the formula I



or a water-soluble salt thereof.

Suitable salts listed in the above Application are water-soluble salts or partial salts, for example, of an alkali metal, an alkaline earth metal, or a C₁-C₂₀alkylamine optionally substituted with one to six hydroxyl groups. Specific salts listed are salts of lithium, sodium, potassium, calcium, strontium, magnesium, ammonia, methylamine, ethylamine, n-propylamine, trimethylamine, triethylamine, n-butylamine, n-hexylamine, octylamine, ethanolamine and triethanolamine.

These salts are merely listed as alternatives to the free acid form of 2-hydroxyphosphonoacetic acid: there is no suggestion that any synergistic effects could be obtained by employing specific metal ions in combination with 2-hydroxyphosphonoacetic acid, nor is there any suggestion in GB 2,112,370 A that 2-hydroxyphosphonoacetic acid could be employed to condition metal surfaces against corrosion prior to exposure to a corrosive or scaling environment.

It has now been found that metal surfaces may be conditioned to inhibit their corrosion and/or to inhibit scale deposition thereon if the metal surfaces are treated, prior to contact with a corrosive/scaling system, with 2-hydroxyphosphonoacetic acid or a water-soluble salt thereof and a metal ion.

Moreover, it has also been found, surprisingly, that synergistic effects are obtained when metal surfaces exposed to corrosion and/or scale deposition are treated during contact with an aqueous corrosive scaling system, with a combination of 2-hydroxyphosphonoacetic acid and certain metal ions.

Accordingly, the present invention relates to a process for conditioning metal surfaces, in particular iron or copper surfaces (or surfaces of their corresponding alloys) to inhibit their corrosion and/or to inhibit scale deposition thereon by

- A) treating said surfaces prior to contact with a corrosive or scaling environment, with a) 2-hydroxyphosphonoacetic acid or a water-soluble salt thereof and b) a metal ion from the series of one or more of cobalt, iron, barium, calcium, zinc, chromium, nickel, strontium, manganese, cadmium, cerium or magnesium ions or
- B) treating said surfaces during contact with an aqueous system capable of corroding the metal surfaces or depositing scale thereon, with a combination of:
 - a) 2-hydroxyphosphonoacetic acid or a water-soluble salt thereof and
 - b) a metal ion from the series of one or more of cobalt, iron, barium, zinc, chromium, nickel, manganese, cadmium or cerium ions.

Treatments A) and B) can advantageously be applied by cathodically polarizing the metal surface to be treated, for example, by any of the conventional impressed current techniques, which can be found for example in Chapter II of "Corrosion" by L.L. Schreir, Newnes-Butterworth 1976.

With respect to the treatments effected under heading A), the surface to be treated may be contacted, for example, with an aqueous

solution of 2-hydroxyphosphonoacetic acid (or a water-soluble salt thereof) in combination with the metal ion b) which imparts synergistic corrosion inhibiting and/or scale inhibiting effects in combination with 2-hydroxyphosphonoacetic acid.

Some typical applications of treatments A) with the preferred application of impressed current techniques include temporary protection of metal surfaces to be exposed to corrosive atmospheres, for example ambient atmospheres; pre-treatment of metal surfaces to be subsequently painted; co-treatment in order to seal a phosphated metal surface; and formulating a paint containing 2-hydroxyphosphonoacetic acid (or a salt thereof) and the metal ion b) and then applying this paint onto the metal surface to be conditioned, for example by spraying, brushing, dipping or cathodic electrodeposition.

In each of these typical applications of treatments of type A), the metal surface, for example a phosphated ingot steel (mild steel) surface, may be immersed in a solution containing 2-hydroxyphosphonoacetic acid (or a water-soluble salt thereof) and a metal ion b), as hereinbefore defined, or said solution may be painted or sprayed onto the said phosphated metal surface.

With respect to sealing of phosphated metal surfaces, it is common practice to phosphate the surface of metal articles to form a bonding or keying layer since protective or decorative paint coats the metal articles, and to minimise subsequent corrosion under the finish. The term 'phosphating' is applied to the treatment of the metal surface in solutions which form a coating consisting mainly of metal phosphates. Such coatings, while forming a good key for the paint finish, are generally not entirely satisfactory in inhibiting subsequent corrosion due to the porosity of the phosphate coating. It is therefore customary to improve said corrosion inhibition by sealing the phosphate coating, traditionally by immersion in an aqueous chromate solution. However, the use of chromate solutions presents toxicity and effluent problems; therefore, there is a need to find new sealing techniques which avoid the disadvantages associated with chromate sealing. It has been found

that the application of a type A conditioning according to the invention provides effective phosphate sealing, optionally in combination with cathodizing the phosphated metal surface, and avoids the problems associated with conventional chromate treatments.

In relation to the electropainting technique, the initial coating of paint or polymer applied to the surface of metal articles, either directly onto the metal surface or after phosphating, is commonly an electropaint. Electropaints are coating compositions which are emulsifiable or soluble in water. These compositions can be caused to be deposited onto a metal surface by polarizing said metal surface, either anodically or cathodically relative to the other electrode, according to the type of paint used. When a cathodically applied electropaint is deposited, the corrosion resistance of the coated metal may be enhanced by simultaneously conditioning the metal surface, or sealing the phosphate coating, according to the type A embodiment of the present invention, by incorporating 2-hydroxyphosphonoacetic acid (or a water-soluble salt thereof) in combination with the synergistic metal ion b), into the electropaint composition.

In treatments according to the invention under heading A or B, the metal ion may be used as an independent metal salt or as the pre-formed salt of the compound of the formula I, or a combination of the two.

Some metal ions b), such as cobalt, iron and barium ions, which provide very effective synergistic combinations with the compound of the formula I, are generically embraced in British Patent Application 2,112,370 A.

Moreover, the above British Patent Application does not suggest that the use of the compound of the formula I, in the form of a water-soluble salt, could lead to much improved results over and above the results to be obtained using the free acidic form of the compound of the formula I.

2-Hydroxyphosphonoacetic acid is a known compound which has been described in U.S. Patent 3,032,500 and, more recently, in European Patent Application 27,199. It can be prepared by known methods, for example by

reacting orthophosphoric acid, a salt or a solution thereof, or phosphorus trichloride (or PCl_3 /water mixtures) with glyoxylic acid, a salt or a solution thereof.

The ratio of 2-hydroxyphosphonoacetic acid (or a water-soluble salt thereof) to the metal ion b), used in the corrosion- and/or scale-inhibiting combinations employed in the conditioning processes according to the invention, may vary within wide limits, e.g. from 100:1 to 1:100, more preferably from 10:1 to 1:10 parts by weight.

In practice, the amount of the combination of 2-hydroxyphosphonoacetic acid and the metal ion which is used to treat the metal surface, for example by adding the combination to the aqueous system in contact with the metal surface varies depending upon the protective function which the combination is required to perform. For corrosion-inhibiting protective treatments, optionally in combination with scale inhibiting treatments, the amount of said combination added to the aqueous system is usually within the range of from 0.1 to 50,000 ppm (or 0.00001 to 5% by weight), preferably from 1 to 500 ppm (or 0.0001 to 0.05% by weight), and, for example, from 1 to 100 ppm (or 0.0001 to 0.01% by weight), based on the aqueous system. For solely anti-scale purposes, the amount of said combination used is usually from 1 to 200 ppm, preferably 1 to 30 ppm, based on the aqueous system.

With respect to aqueous systems by which a metal surface may be conditioned according to the present invention, of particular interest with respect to combined corrosion inhibition and anti-scale treatments are cooling-water systems, steam-generating systems, sea-water evaporators, hydrostatic boilers, gas scrubbing systems, closed-circuit heating systems, water-based refrigeration systems and oil field applications; for corrosion inhibition treatments alone, aqueous systems of particular interest include aqueous machining fluid formulations (e.g. for use in boring, milling, reaming, broaching, drawing, spinning, turning, cutting, sawing, grinding, and thread-cutting operations or in non-cutting shaping in drawing or rolling operations), aqueous scoring systems, engine cooling systems, aqueous glycol antifreeze systems, water/glycol

hydraulic fluids and water-based surface-coating systems.

In the particular case of the inhibition of scale and corrosion in oil field applications, special problems are presented which are not encountered in more conventional water treatment applications. Thus, formation water, associated with oil-bearing strata, often contains barium and strontium as well as ions such as calcium, magnesium, carbonate and bicarbonate ions which are more commonly found in surface waters and sea water. Therefore, in situations in which surface or sea water becomes mixed with formation water, severe scaling can occur due to the precipitation of barium sulfate, strontium sulfate, calcium carbonate and mixtures thereof. This type of scaling occurs, for example, during cooling/depressurization (in the formation) of recovered crude oil/water emulsions in the rock formation in the well base and in the well bore when water is pumped into the formation to "squeeze" a well. This type of scale formation can be effectively inhibited by the conditioning technique according to the present invention.

In addition to inhibiting the deposition of conventional scale onto metal surfaces, the conditioning process according to the present invention is also useful in inhibiting deposition of calcium - or magnesium silicate scale.

The synergistic inhibitor combination may be used alone or in conjunction with other compounds known to be useful in the treatment of aqueous systems.

Wholly aqueous systems to which the process of the present invention may be applied, include cooling-water systems, air-conditioning systems, steam-generating systems, sea-water evaporator systems, hydrostatic cookers, and closed-circuit heating or refrigerant systems; further corrosion inhibitors may be used, such as, for example, water soluble zinc salts; phosphates; polyphosphates; phosphonic acids and their salts, for example, acetodiphosphonic acid, nitrilotrismethylenephosphonic acid and methylaminodimethylene phosphonic acid; other phosphonocarboxylic acids and their salts, for example, those described in German

Offenlegungsschrift 2,632,774, 2-phosphonobutane-1,2,4-tricarboxylic acid and those disclosed in GB 1,572,406; chromates, for example sodium chromate; nitrates, for example sodium nitrate; nitrites, for example sodium nitrite; molybdates, for example sodium molybdate; silicates, for example sodium silicate; benzotriazoles, 5,5-methylenebis-benzotriazole or copper-deactivating benzotriazoles or tolutriazole derivatives; N-acylsarcosines; N-acryliminodiacetic acids; ethanolamines; fatty acid amines; and polycarboxylic acids, for example polymaleic acid and polyacrylic acid, as well as their respective alkali metal salts, copolymers of maleic anhydride, copolymers of acrylic acid, and substituted derivatives of polymaleic and polyacrylic acids and their copolymers.

Moreover, in such completely aqueous systems, the synergistic inhibitor combination may be used in conjunction with further dispersing and/or anti-settling agents, for example polymerized acrylic acid (or its salts), phosphinopolycarboxylic acids (as described in British Patent 1,458,235), hydrolysed polyacrylonitrile, polymerized methacrylic acid and its salts, polyacrylamide and copolymers (thereof) from acrylic and methacrylic acids, lignin sulphonic acid and its salts, tannin, naphthalenesulphonic acid/ formaldehyde condensation products, starch and its derivatives, cellulose, acrylic acid/lower alkylhydroxyacrylate copolymers such as those described in U.S. Patent 4,029,577, sulfonated styrene/maleic anhydride copolymers, styrene/maleic anhydride copolymers and sulfonated homopolymers such as those described in the U.S. Patent 4,374,733 and combinations thereof. Specific anti-settling agents, such as, for example, 2-phosphonobutane-1,2,4-tricarboxylic acid, acetodiphosphonic acid, hydrolysed polymaleic anhydride and its salts, alkylphosphonic acids, 1-aminoalkyl-1,1-diphosphonic acids and their salts, and alkali metal polyphosphates, may also be used.

Precipitating agents such as alkali metal orthophosphates, carbonates; oxygen scavengers, such as alkali metal sulfites and hydrazines; sequestering agents, such as nitrilotriacetic acid and its salts; antifoaming agents, such as silicones, for example polydimethylsiloxanes, distearylsebacamide, distearyl adipamide and related products derived

from ethylene oxide and/or propylene oxide condensations, in addition to fatty alcohols, such as capryl alcohols and their ethylene oxide condensation products; and biocides, for example amines, quaternary ammonium compounds, chlorophenols, sulfur-containing compounds such as sulfones, methylenebisthiocyanates and carbamates, triazines, phosphonium compounds, chlorinated and chlorine-release agents and organometallic compounds, such as tributyltin oxide, may be used.

If the metal conditioned by the method according to the invention is treated from a system which is not completely aqueous, for example an aqueous machining fluid formulation, it may be, for example, a water-dilutable cutting or grinding fluid.

The aqueous machining fluid formulations of the invention may be, for example, metal working formulations. By "metal working" we mean "reaming, broaching, drawing, spinning, cutting, grinding, boring, milling, turning, sawing, chipless shaping or rolling". Examples of water-soluble cutting or grinding fluids into which the corrosion inhibiting combination may be incorporated include:

- a) Aqueous concentrates of one or more corrosion inhibitor, and optionally one or more anti-wear additives, used at dilutions of 1:50 to 1:100, which are usually employed as grinding fluids;
- b) Polyglycols containing biocides, corrosion inhibitors and anti-wear additives which are used at dilutions of 1:20 to 1:40 for cutting operations and 1:60 to 1:80 for grinding;
- c) Semi-synthetic cutting fluids similar to (b) but containing in addition 10 to 25% of oil with sufficient emulsifier to render the water-diluted product translucent;
- d) An emulsifiable mineral oil concentrate containing, for example, emulsifiers, corrosion inhibitors, extreme pressure/anti-wear additives, biocides, antifoaming agents, coupling agents, etc.; they are generally diluted from 1:10 to 1:50 with water to a white opaque emulsion;

e) Products similar to (d) containing less oil and more emulsifier which on dilution to concentrations of 1:50 to 1:100 give translucent emulsions for cutting or grinding operations.

For those partly aqueous systems in which the aqueous system component is an aqueous machining fluid formulation, the synergistic inhibitor combination may be used singly or in admixture with other additives, for example known further inhibitors and/or extreme-pressure additives.

Examples of other corrosion inhibitors which may be used in this aqueous system, in addition to the inhibitor combination used according to the invention, include the following groups:

a) Organic acids, their esters or ammonium, amine, alkanolamine and metal salts, for example, benzoic acid, p-tert-butylbenzoic acid, disodium sebacate, triethanolamine laurate, iso-pelargonic acid, triethanolamine salt of p-toluenesulphonamidocaproic acid, sodium N-lauroylsarcosinate or nonyl-phenoxyacetic acid;

b) Nitrogen-containing materials, such as the following types: fatty acid alkanolamides; imidazolines, for example, 1-hydroxyethyl-2-oleylimidazoline; oxazolines; triazoles, for example, benzotriazoles; triethanolamine; fatty acid amines; and inorganic salts, for example sodium nitrate.

c) Phosphorus-containing materials, such as the following types: amine phosphates, phosphonic acids or inorganic salts, for example, sodium dihydrogen phosphates or zinc phosphate;

d) Sulfur-containing compounds, such as the following types: sodium, calcium or barium petroleum sulfonates, or heterocycles, for example sodium mercaptobenzothiazole.

Nitrogen-containing materials, particularly triethanolamine, are preferred.

Examples of extreme pressure additives which may be present in the systems treated according to the present invention, include sulfur and/or

phosphorus- and/or halogen-containing materials, for example sulfurized sperm oil, sulfurized fats, tritolyl phosphate, chlorinated paraffins or ethoxylated phosphate esters.

When triethanolamine is present in the aqueous systems treated according to the present invention, it is preferably present in an amount such that the ratio of synergistic inhibitor combination to triethanolamine is from 2:1 to 1:20.

The partly aqueous systems for which the process of the present invention may be applied, may also be aqueous surface-coating compositions, for example emulsion paints and aqueous powder coatings for metallic substrates.

The aqueous surface-coating composition may be, for example, a paint such as a styrene-acrylic copolymer emulsion paint, a resin, latex, or other water-based polymer surface-coating systems used to coat a metal substrate. The inhibitor combination according to the present invention may be used to prevent rapid rusting of the metal substrate during application of the surface coating and to prevent subsequent corrosion during use of the coated metal.

In aqueous surface-coating compositions treated by the method of the invention, the inhibitor combination may be used singly or in admixture with other additives, for example known corrosion inhibitors, biocides, emulsifiers and/or pigments.

The further known corrosion inhibitors which may be used are, for example, those of classes a), b), c) and d) hereinbefore defined.

Examples of biocides which may be used in the aqueous systems treated according to the invention, include the following: phenols and alkylated and halogenated phenols, for example pentachlorophenol, o-phenylphenol, o-phenoxyphenol and chlorinated o-phenoxyphenol, and salicylanilides, diamines, triazines and organometallic compounds, such as organomercury compounds and organotin compounds.

Examples of pigments which may be used in the aqueous systems treated according to the invention include titanium dioxide, zinc chromate, iron oxide and organic pigments such as the phthalocyanines.

The following examples further illustrate the present invention. The 2-hydroxyphosphonoacetic acid, the active ingredient used in examples 2 to 24 [sic] is prepared as follows:

Example 1: A) 16.3 parts (0.11 mole) of 50% aqueous glyoxylic acid and 8.2 parts (0.1 mole) of orthophosphoric acid are heated together with stirring at 98-100°C for 24 hours to give 24.5 parts of 60% aqueous 2-hydroxyphosphonoacetic acid.

B) 150 parts of a 60% aqueous solution of 2-hydroxyphosphonoacetic acid obtained according to Example 1A are evaporated under reduced pressure (20 millibars) to give 104 parts of a viscous brown oil. This oil is induced to crystallize. The crude crystalline mass is then triturated with acetone to remove impurities. The resulting buff-coloured crystalline 2-hydroxyphosphonoacetic acid is removed by filtration, washed with acetone and dried.

The crude crystalline 2-hydroxyphosphonoacetic acid so obtained is then recrystallized from water to give pure 2-hydroxyphosphonoacetic acid as white crystals m.p. 165 - 167°C.

^{31}P -NMR): $\delta = -14$ ppm (relative to external standard H_3PO_4):

^1H -NMR: $\text{P}-\underline{\text{CH}}\delta = 4.24 \text{ cm}^{-1}$

$J_{\text{P}-\text{CH}} = 18 \text{ Hz}$

IR: COOH : 1745 cm^{-1} ; P=O ; 1200 cm^{-1} .

Examples 2 to 8: Corrosion inhibitor activity of the active inhibitor combination is demonstrated in the following way:

Mild steel coupons, 5 cm x 2.5 cm are scrubbed with pumice, immersed for one minute in hydrochloric acid and then rinsed, dried and weighed.

The desired proportion of additive combination is dissolved in 200 ml of

deionized water. The metal ions are added as their chlorides and all test solutions are adjusted to pH 7 with sodium hydroxide solution. A steel coupon prepared as described above is suspended in the solution and the whole is stored in a closed bottle in a thermostat at 40°C. During the storage period, air is passed through the solution at 500 ml/minute, the passage of air being screened from the steel coupon; any water losses by evaporation are replaced with deionized water.

After 48 hours, the steel coupons are withdrawn, scrubbed without pumice, immersed for one minute in hydrochloric acid inhibited with 1% by weight of hexamine and then rinsed, dried and reweighed. A certain loss in weight will have occurred. The results obtained in a series of tests using 100 ppm each of 2-hydroxyphosphonoacetic acid and various metal ions are set out in Table 1, in which m/d/d, denotes milligrams weight loss/sq. decimetre/day:

Table 1

<u>Example</u>	<u>Metal ion</u>	<u>Corrosion (m/d/d)</u>
Control	Sodium	140
Control	Potassium	124
2	Zinc	1.6
3	Cadmium	2.0
4	Manganese	2.0
5	Cobalt	2.2
6	Nickel	2.4
7	Barium	6.8
8	Titanium	84

When the above metal ions are used in the above test methods in the absence of 2-hydroxyphosphonoacetic acid, the corrosion values (m/d/d) obtained are each of the order of 80-120.

Examples 9 to 15: The synergistic effect of combinations of 2-hydroxyphosphonoacetic acid and metal ions, used according to the invention, is assessed by determining the reduction of cathodic current of a metal surface conditioned with said combination. In order to effect this assessment, the final steady-state current of the conditioned metal surface is measured in air-saturated water.

A mild steel rotating disc electrode, rotating at 4 Hz, is held at -800 mV (relative to a standard calomel electrode) in the test solution, and the final steady-state current is recorded using a conventional three-electrode potentiostatic circuit.

The test solutions used contain 0.1 M sodium perchlorate as background electrolyte and either:

- a) 100 ppm of 2-hydroxyphosphonoacetic acid prepared as in Example 1;
or
- b) 100 ppm of 2-hydroxyphosphonoacetic acid (HPAA) and
100 ppm of a metal ion component (as its chloride).

The results in Table 2 below clearly show the reduction in the current passed at -800 mV when using 2-hydroxyphosphonoacetic acid in combination with a metal ion, relative to the use of 2-hydroxyphosphonoacetic acid alone.

Table 2

<u>Example</u>	<u>Inhibitor</u>	<u>Metal ion</u>	<u>Cathodic current (μAcm^{-2})</u>
9	100 ppm HPAA	100 ppm Iron	29
- 10	- HPAA	Barium Barium	487 31
11	HPAA	Chromium	60
- 12	- HPAA	Chromium Chromium	474 101
13	HPAA	Manganese	114
14	HPAA	Cadmium	200
15	HPAA	Cerium	270

This decrease in current passed is indicative of:

i) a decrease in the rate of oxygen reduction at the metal surface with the consequent anticipation that there will be a degree of correlation between these data and the corrosion inhibition data of Example 2 relating to freely corroding metal coupons. This correlation will not be complete, however, because the potential of -800 mV applied in the test of Examples 9 to 15 suppresses the effect of anodic processes;

ii) a decrease in the current required to prevent corrosion by the use of an impressed cathodic current; and

iii) the conditioning of the treated metal surface by cathodic polarization in solutions of HPAA and HPAA combined with synergistic metal ions.

Example 16: A mild steel coupon (2.5 cm x 5 cm) is immersed in a solution

containing 100 ppm of HPAA and 100 ppm of Ca^{++} , and a cathodic current of $50 \mu\text{Acm}^{-2}$ is passed through the coupon for 22 hours. The coupon is then removed from the solution, washed with distilled water and dried.

The coupon so conditioned, together with similar, clean, untreated coupons, is suspended near the top of a 2 litre beaker containing 200 ml of deionized water, the atmosphere of which is held at 100% relative humidity and at 40°C by means of a hot plate placed below the beaker and a cooling coil arranged around the top half of the beaker. Vapour condenses on each of the suspended coupons and causes corrosion there. After 24 hours exposure of the coupons to the steam, the surface of the untreated coupons is covered with spots (0.5 mm) of rust. The coupon pre-conditioned according to the process of the invention, is free of rust spots to an extent of 80%. The remaining 20% of the surface of the pre-conditioned coupon is evenly corroded but to a lesser extent than the control coupons.

Example 17: Scale formation on metal surfaces can be initiated at cathodic corrosion sites. Therefore an accelerated test to demonstrate the effectiveness of 2-hydroxyphosphonoacetic acid for preventing scale formation from water containing barium, strontium and sulfate ions is carried out by cathodically polarizing a mild steel specimen in the scaling water. The specimen is held at -800 mV with respect to a standard calomel electrode, and the change in current and change in visual appearance is monitored with respect to time. The test solution is used at 40°C and consists of equal parts of filtered sea water and a solution in deionized water of the following salts:

	<u>g/l</u>
Calcium chloride 6 H_2O	17.5
Magnesium chloride 6 H_2O	5.0
Barium chloride 2 H_2O	0.5
Strontium nitrate	1.6
Sodium chloride	77.0
Potassium chloride	2.0
Sodium carbonate	0.5

During a 15 minute test period, the metal specimen becomes coated with a white scale of barium and strontium sulfate and the cathodic current passed through the specimen drops due to the formation of a thin scale layer. A similar experiment is carried out, except that 15 parts per million of 2-hydroxyphosphonoacetic acid are added to the test solution. The current passed through the specimen again drops due to the conditioning of the metal surface according to the process of the invention, but the surface remains completely free from scale.



Patent claims

1. A process for conditioning metal surfaces, in particular iron or copper surfaces (or surfaces of their corresponding alloys) to inhibit their corrosion and/or to inhibit scale deposition thereon by
 - A) treating said surfaces prior to contact with a corrosive or scaling environment, with a) 2-hydroxyphosphonoacetic acid or a water-soluble salt thereof and b) a metal ion from the series of one or more of cobalt, iron, barium, calcium, zinc, chromium, nickel, strontium, manganese, cadmium, cerium or magnesium ions or
 - B) treating said surfaces during contact with an aqueous system capable or corroding the metal surfaces or depositing scale thereon, with a combination of:
 - a) 2-hydroxyphosphonoacetic acid or a water-soluble salt thereof and
 - b) a metal ion from the series of one or more of cobalt, iron, barium, zinc, chromium, nickel, manganese, cadmium or cerium ions.
2. A process according to claim 1 wherein the metal surfaces to be treated are cathodically polarized.
3. A process according to claim 1 wherein the metal surface, prior to contact with a corrosive environment, is treated with an aqueous solution of 2-hydroxyphosphonoacetic acid (or a water-soluble salt thereof) and with a metal ion b), as defined in claim 1.
4. A process according to claim 3 wherein the metal ion b) imparts synergistic corrosion-inhibiting and/or scale-inhibiting effects in combination with 2-hydroxyphosphonoacetic acid, and is used in the form of a metal salt.
5. A process according to claim 3 whereby temporary protection of metal surfaces which are exposed to a corrosive atmosphere is effected by pretreatment of the metal surfaces, prior to contact with a corrosive environment, by painting or by co-treatment, where the metal surfaces are phosphated and provided with a protective coat of paint or by



formulating a paint containing 2-hydroxyphosphonoacetic acid (or a water-soluble salt thereof) and a metal ion b), and then applying this paint onto the metal surface to be conditioned.

6. A process according to claim 1 wherein the ratio of 2-hydroxyphosphonoacetic acid (or a water-soluble salt thereof) to metal ion b) as defined in claim 1 is within the range of from 100:1 to 1:100.

7. A process according to claim 6 wherein the ratio of 2-hydroxyphosphonoacetic acid (or a water-soluble salt thereof) to metal ion b) is between 10:1 and 1:10.

8. A process according to claim 1 wherein the inhibitor combination a) and b) is used in an aqueous system, in contact with a metal surface which requires corrosion-inhibiting and optionally scale-inhibiting protective treatment, in an amount of from 1 to 500 ppm, based on the aqueous system.

9. A process according to claim 8 wherein the inhibitor combination a) and b) is employed in an amount of from 1 to 100 ppm, based on the aqueous system.

10. A process according to claim 1 wherein the inhibitor combination a) and b) is employed in an aqueous system in contact with a metal surface which requires only scale-inhibiting treatment, in an amount of from 1 to 200 ppm, based on the aqueous system.

11. A process according to claim 10 wherein the inhibitor combination a) and b) is added to the aqueous system in an amount of from 1 to 30 ppm, based on the aqueous system.

12. A process according to claim 10 wherein the aqueous system is in contact with the metal surface which requires only a corrosion inhibition system and is an aqueous machining fluid formulation, an aqueous scouring system, an aqueous glycol antifreeze system, a water/glycol hydraulic fluid or a water-based surface coating composition.



13. A process according to claim 12 wherein the aqueous machining fluid formulation is a water-soluble cutting or grinding fluid.

14. A process according to claim 1, wherein the aqueous system is in contact with a metal surface which requires a combined corrosion inhibition and anti-scale treatment and is a cooling-water system, a steam-generating system, a sea-water evaporator, a hydrostatic boiler, a gas scrubbing system, a closed-circuit heating system, a water-based refrigeration system or an oil field application system.

15. A process according to claim 1 wherein the inhibitor combination a) and b) is used alone or in conjunction with other compounds known to be useful in the treatment of wholly or partly aqueous systems.

16. A process according to claim 15 wherein the aqueous system is a wholly aqueous system and is a cooling-water system, an air-conditioning system, a steam-generating system, a sea-water evaporator, a hydrostatic boiler, a gas scrubbing system or a closed-circuit heating or refrigeration system and wherein the inhibitor combination a) and b) is used in conjunction with one or more further corrosion inhibitors, a dispersing and/or anti-precipitation agent, a precipitating agent, an oxygen scavenger, a sequestering agent, an antifoaming agent and a biocide.

17. A process according to claim 15 wherein the partly aqueous system is an aqueous surface-coating composition and wherein the inhibitor combination a) and b) is used in conjunction with one or more corrosion inhibitors, a biocide, an emulsifier and/or a pigment.

18. A process according to claim 15 wherein the aqueous system is only partly aqueous and is an aqueous machining fluid and wherein the inhibitor combination a) and b) is used in conjunction with one or more further corrosion inhibitors and/or an extreme pressure additive.

19. A process according to claim 18 wherein the further corrosion inhibitor is triethanolamine.



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20. A process according to claim 19 wherein triethanolamine is present in an amount such that the ratio of inhibitor combination a) and b) to triethanolamine is from 2:1 to 1:20,

21. A metal surface conditioned by a process according to claim 1.



As printed

Claims

1. Process for conditioning metal surfaces, in particular iron or copper surfaces (or surfaces of their corresponding alloys) to inhibit their corrosion and/or to inhibit scale deposition thereon by
 - A) treating said surfaces prior to contact with a corrosive or scaling environment, with
 - a) 2-hydroxyphosphonoacetic acid or water-soluble salt thereof and
 - b) a metal ion from the series of one or more of cobalt, iron, barium, calcium, zinc, chromium, nickel, strontium, manganese, cadmium, cerium or magnesium ions or
 - B) treating said surfaces during contact with an aqueous system capable of corroding the metal surfaces or depositing scale thereon, with a combination of :
 - a) 2-hydroxyphosphonoacetic acid or a water-soluble salt thereof and
 - b) a metal ion from the series of one or more of cobalt, iron, barium, zinc, chromium, nickel, manganese, cadmium or cerium ions.
2. Process according to claim 1, wherein the metal surfaces to be treated are cathodically polarised.
3. Process according to claim 1 wherein the metal surface, prior to contact with a corrosive environment, is treated with an aqueous solution of 2-hydroxyphosphonoacetic acid (or a water-soluble salt thereof) and with a metal ion b), as defined in claim 1.
4. Process according to claim 3, wherein the metal ion b) imparts synergistic corrosion-inhibiting and/or scale-inhibiting effects in combination with 2-hydroxyphosphonoacetic acid, and is used in the form of a metal salt.
5. Process according to claim 3 whereby temporary protection of metal surfaces which are exposed to a corrosive atmosphere is effected by pretreatment of the metal surfaces, prior to contact with a corrosive environment, by painting or by co-treatment, where the metal surfaces are phosphated and provided with a protective coat of paint or by formulating a paint containing 2-hydroxyphosphonoacetic acid (or a water-soluble salt thereof) and a metal ion b), and then applying this paint onto the metal surface to be conditioned.
6. Process according to claim 1 wherein the ratio of 2-hydroxyphosphonoacetic acid (or a water-soluble salt thereof) to metal ion b) as defined in claim 1 is within the range of from 100 : 1 to 1 : 100.
7. Process according to claim 6 wherein the ratio of 2-hydroxy-phosphonoacetic acid (or water-soluble salt thereof) to metal ion b) is between 10 : 1 and 1 : 10.
8. Process according to claim 1 wherein the inhibitor combination a) and b) is used in an aqueous system, in contact with a metal surface which requires corrosion-inhibiting and optionally scale-inhibiting protective treatment, in an amount of from 1 to 500 ppm, based on the aqueous system.
9. A process according to claim 8 wherein the inhibitor combination a) and b) is employed in an amount of from 1 to 100 ppm based on the aqueous system.
10. A process according to claim 1 wherein the inhibitor combination a) and b) is employed in an aqueous system in contact with a metal surface which requires only a scale-inhibiting treatment, in an amount of from 1 to 200 ppm, based on the aqueous system.



11. A process according to claim 10 wherein the inhibitor combination a) and b) is added to the aqueous system in an amount of from 1 to 30 ppm, based on the aqueous system.
12. A process according to claim 10 wherein the aqueous system is in contact with a metal surface which requires only a corrosion inhibition system and is an aqueous machining fluid formulation, an aqueous scouring system, an aqueous glycol antifreeze system, a water/glycol hydraulic fluid or a water-based surface coating composition.
13. A process according to claim 12 wherein the aqueous machining fluid formulation is a water-soluble cutting or grinding fluid.
14. A process according to claim 1, wherein the aqueous system is in contact with a metal surface which requires a combined corrosion inhibition- and anti-scale treatment and is a cooling-water system, a steam-generating system, a sea water evaporator, a hydrostatic boiler, a gas-scrubbing system, a closed-circuit heating system, an aqueous-based refrigeration system or an oil field system.
15. A process according to claim 1 wherein the inhibitor combination a) and b) is used alone or in conjunction with other compounds known to be useful in the treatment of wholly or partly aqueous systems.
16. A process according to claim 15 wherein the aqueous system is a wholly aqueous system and is a cooling-water system, an air-conditioning system, a steam-generating system, a sea-water evaporator, a hydrostatic boiler, a gas-scrubbing system or a closed-circuit heating or refrigeration system and wherein the inhibitor combination a) and b) is used in conjunction with one or more further corrosion inhibitors, a dispersing and/or anti-precipitation agent, a precipitating agent, an oxygen scavenger, a sequestering agent, an anti-foaming agent and a biocide.
17. A process according to claim 15 wherein the partly aqueous system is an aqueous surface-coating composition and wherein the inhibitor combination a) and b) is used in conjunction with one or more corrosion inhibitors, a biocide, an emulsifier and/or a pigment.
18. A process according to claim 15 wherein the aqueous system is only partly aqueous and is an aqueous machining fluid and wherein the inhibitor combination a) and b) is used in conjunction with one or more further corrosion inhibitors and/or an extreme pressure additive.
19. A process according to claim 18 wherein the further corrosion inhibitor is triethanolamine.
20. A process according to claim 19 wherein triethanolamine is present in an amount such that the ratio of inhibitor combination a) and b) to triethanolamine is from 2 : 1 to 1 : 20.
21. Metal surfaces conditioned by a process according to claim 1.

Revendications

1. Procédé pour traiter des surfaces métalliques, en particulier des surfaces de fer ou de cuivre (ou leurs alliages correspondants) pour en inhiber la corrosion et/ou empêcher des dépôts de tartre, procédé caractérisé en ce que
 - A) On traite ladite surface, avant qu'elle ne vienne en contact avec un environnement corrosif et générateur de tartre avec
 - a) de l'acide hydroxy-2 phosphonacétique ou un sel hydrosoluble de cet acide, et
 - b) un ion métallique choisi dans le groupe comportant un ou plusieurs ions cobalt, fer, baryum, calcium, zinc, chrome, nickel, strontium, manganèse, cadmium, cérium ou magnésium, ou bien
 - B) On traite ladite surface pendant son contact avec une composition aqueuse pouvant corroder la surface métallique ou y provoquer le dépôt de tartre, avec une combinaison :
 - a) d'acide hydroxy-2 phosphonacétique ou d'un sel hydrosoluble de cet acide, et
 - b) d'un ion de métal choisi parmi un ou plusieurs ions cobalt, fer, baryum, zinc, chrome, nickel, manganèse, cadmium ou cérium.
2. Procédé selon la revendication 1, caractérisé en ce que les surfaces métalliques à traiter sont soumises à polarisation cathodique.
3. Procédé selon la revendication 1, caractérisé en ce que, avant la venue de la surface métallique en contact avec un environnement corrosif, on traite cette surface par une solution aqueuse d'acide hydroxy-2 phosphonacétique (ou d'un sel hydrosoluble de cet acide) et d'un ion de métal b) tel que défini à la revendication 1.
4. Procédé selon la revendication 3, dans lequel l'ion métallique b), en combinaison avec l'acide hydroxy-2 phosphonacétique, exerce des effets synergiques d'inhibition de la corrosion et/ou d'inhibition de la formation de tartre et est utilisé sous forme d'un sel de métal.
5. Procédé selon la revendication 3, dans lequel on effectue une protection temporaire des surfaces métalliques exposées à une atmosphère corrosive, en effectuant le traitement préliminaire des surfaces métalliques, avant qu'elles ne viennent en contact avec un environnement corrosif, par enduction au pinceau ou par co-traitement, en phosphatant les surfaces métalliques et en les munissant d'une couche de peinture protectrice, ou en formulant une peinture qui contient l'acide hydroxy-2 phosphonacétique (ou un sel hydrosoluble de cet acide) et un ion de métal b), et en utilisant ensuite cette peinture sur la surface métallique à traiter pour la protéger.
6. Procédé selon la revendication 1, dans lequel le rapport entre l'acide hydroxy-2 phosphonacétique



(ou un sel hydrosoluble de cet acide) et l'ion métallique b), tel que défini la revendication 1, se situe entre 100 : 1 et 1 : 100.

7. Procédé selon la revendication 6, dans lequel le rapport entre l'acide hydroxy-2 phosphonacétique (ou un sel hydrosoluble de cet acide) et l'ion métallique b), se situe entre 10 : 1 et 1 : 10.

8. Procédé selon la revendication 1, dans lequel on utilise la combinaison inhibitrice a) et b) dans une composition aqueuse, qui vient en contact avec une surface métallique rendant nécessaire un traitement de protection contre la corrosion et éventuellement d'inhibition de la formation de tartre, en une quantité de 1 à 500 ppm, par rapport à la composition aqueuse.

9. Procédé selon la revendication 8, dans lequel on utilise la combinaison inhibitrice a) et b) en une quantité de 1 à 100 ppm, par rapport à la composition aqueuse.

10. Procédé selon la revendication 1, dans lequel on utilise la combinaison inhibitrice a) et b) dans une composition aqueuse qui est en contact avec une surface métallique, ne rendant nécessaire qu'un traitement d'inhibition de la formation du tartre, en une quantité de 1 à 200 ppm, par rapport à la composition aqueuse.

11. Procédé selon la revendication 10, dans lequel on introduit en une quantité de 1 à 30 ppm, par rapport à la composition aqueuse, la combinaison inhibitrice a) et b) dans la composition aqueuse.

12. Procédé selon la revendication 10, dans lequel la composition aqueuse vient en contact avec la surface métallique en ne nécessitant qu'une inhibition de la corrosion et dans lequel une composition ou formulation aqueuse est un liquide servant au traitement d'usinage, une composition aqueuse pour épuration ou purification, une composition aqueuse de circuit anti-gel contenant du glycol, un liquide hydraulique eau/glycol ou une composition à base d'eau pour l'enduction ou le revêtement des surfaces.

13. Procédé selon la revendication 12, dans lequel la formulation de liquide aqueux pour le traitement d'usinage est un liquide hydrosoluble de coupe ou de rectification.

14. Procédé selon la revendication 1, dans lequel la composition aqueuse est en contact avec une surface métallique exigeant un traitement combiné d'inhibition de la corrosion et anti-tartre, et la composition aqueuse est celle d'un circuit d'eau de refroidissement, d'un circuit ou dispositif de production de vapeur d'eau, d'un appareillage d'évaporation de l'eau de mer, d'une chaudière hydrostatique, d'un dispositif de lavage de gaz, d'un dispositif de chauffage à circuit fermé, d'un dispositif de refroidissement à base d'eau ou d'un dispositif applicable dans un champ pétrolier.

15. Procédé selon la revendication 1, dans lequel on utilise la combinaison inhibitrice a) et b) isolément ou en combinaison avec d'autres composés que l'on sait être utilisables pour le traitement de systèmes ou circuits entièrement ou partiellement aqueux.

16. Procédé selon la revendication 15, dans lequel le système ou composition aqueux est une composition entièrement aqueuse et représente un système ou dispositif de refroidissement par de l'eau de refroidissement, un circuit d'installation de climatisation, un dispositif de production de vapeur d'eau, un évaporateur d'eau de mer, une chaudière hydrostatique, un dispositif de lavage de gaz ou un dispositif de chauffage ou de refroidissement en circuit fermé, et l'on utilise la combinaison inhibitrice a) et b) avec un ou plusieurs autres inhibiteurs de la corrosion, un agent de dispersion ou un agent anti-précipitation, un agent de précipitation, un produit de fixation de O_2 , un agent de séquestration, un agent anti-mousse ou un biocide.

17. Procédé selon la revendication 15, dans lequel la composition partiellement aqueuse est une composition aqueuse de revêtement de surface, et l'on utilise la combinaison inhibitrice a) et b) en combinaison avec un ou plusieurs inhibiteurs de la corrosion, avec un biocide, avec un émulsifiant et/ou avec un pigment.

18. Procédé selon la revendication 15, dans lequel la composition aqueuse n'est que partiellement aqueuse et est un liquide aqueux servant à l'usinage, et/ou l'on utilise la combinaison inhibitrice a) et b) en combinaison avec un ou plusieurs autres inhibiteurs de corrosion et/ou avec un additif haute pression.

19. Procédé selon la revendication 18, dans lequel l'inhibiteur supplémentaire de la corrosion est la triéthanolamine.

20. Procédé selon la revendication 19, dans lequel la triéthanolamine est présente en une quantité telle que le rapport entre la combinaison inhibitrice a) et b), d'une part, et la triéthanolamine, d'autre part, se situe entre 2 : 1 et 1 : 20.

21. Surfaces métalliques traitées par un procédé de protection selon la revendication 1.