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CORROSION INHIBITING COMPOSITION

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The present invention relates to corrosion inhibition. In particular, the invention is concerned primarily with inhibiting corrosion in water circulation systems where the water comes in contact with ferrous metals such as iron and steel. However, it has also been found very effective for inhibiting corrosion of such metals as copper, brasss, bronze and other non-ferrous metals, and for couples of such metals with ferrous metals.

The invention is an improvement based upon the known fact that phosphates in small added quantities will assist in inhibiting underwater corrosion. In addition, it is known that if a cyanide is added with the phosphates, improved corrosion inhibiting effects are achieved.

The invention stems from the discovery that if chromates are added to phosphates and cyanides in aqueous solution, superior corrosion inhibition results. The beneficial results of the invention may be achieved in solutions containing such corrosive ions as sulphates and chlorides in varying concentrations.

Accordingly it is a principal object of the present invention to furnish an improved corrosion inhibiting composition. An allied object of the invention is to furnish such a corrosion inhibitor which is readily and completely soluble in water.

Another object of the invention is to furnish a corrosion inhibitor which operates to prevent corrosion on ferrous and other metals at elevated temperatures by corrosive water.

Still another object of the invention is to provide a corrosion inhibitor which is adaptable to treat water high in chloride content and/or high in mineral content.

Other objects and advantages will become apparent as the description of the invention and various illustrative embodiments proceeds.

The synergistic anodic corrosion inhibitors illustrative of the invention are prepared by intimately mixing corrosion inhibiting phosphates, including the polyphosphates and orthophosphates, cyanides, complex cyanides or organic nitriles, and chromates. Especially good results have been achieved with monosodium phosphate anhydrous (NaH_2PO_4), sodium ferrocyanide

$$(Na_4Fe(CN)_6.10H_2O)$$

and sodium dichromate hydrous ($Na_2Cr_2O_7.2H_2O$).

Effective commercial compositions within the contemplation of the invention comprise 10 to 40 parts by weight of monosodium phosphate (anhydrous), 25 to 65 parts by weight of sodium dichromate (hydrous), 2 to 25 parts by weight of potassium ferricyanide and the balance commercial sodium sulphate (anhydrous). Although a dry mix of the ingredients has been found satisfactory in a wide variety of commercial applications, the inhibitor may also be packaged in briquette and solution. The present invention contemplates the combination ingredients in whatever form they may be introduced into the system.

In order to evaluate the invention a testing apparatus

and procedure was developed. The testing apparatus comprised a pyrex glass aspirator bottle of four liter capacity serving as a reservoir. Three liters of tap water, or synthetic water adjusted to the desired pH, controlled to include the proper proportion of corrosive material and residual of the inhibitor to be tested were placed within the reservoir. A variable temperature electric heating element in contact with the reservoir was adjusted to maintain the solution therein at a temperature of 150–160° F.

The corrosion test coupon was then inserted in a large tube interposed in the discharge line from the pump circulating from and to the reservoir bottle so that it was in constant contact with the moving fluid. The test coupon was a 3" length of ⅜" diameter cold drawn steel (C–1018) rod with rounded ends. This steel has very nearly the average composition of ordinary black iron pipe. After having been given a suitable surface treatment, the coupons were weighed to the fourth decimal place on an analytical balance.

A rate-of-flow indicator was placed in the circulatory system immediately following the test coupon and the rate adjusted by a needle valve or equivalent device to provide a velocity of fluid passing over the coupon within the range of 0.2 to 0.25 foot per second.

During the runs the pH of the water in the system, the inhibitor residual, and the volume of fluid in the system was adjusted at least twice a day. The rate of flow and temperature of the fluid were checked at more frequent intervals commensurate with maintaining their appropriate operational ranges. All tests were run for five days.

After completing a run, the coupons were then cleaned, dried with a clean cloth, baked in an oven at 110° C. for one hour and cooled in a desiccator. The coupons were then weighed to the fourth decimal place on an analytical balance and the loss of weight determined. The loss of weight was converted to average penetration in inches per year (IPY) according to the accepted formula. This can, of course, be readily converted to mils per year (MPY) by shifting the decimal point.

The following examples, having been evaluated by the test procedure described above, are set forth to further illustrate the invention by way of its detailed application. They are not in any way intended to limit the invention, but rather to point out its widespread usages and equivalent applications. In each case quantities are stated as parts by weight unless otherwise indicated.

EXAMPLE I

A corrosion inhibiting composition was prepared by mixing dry forty (40) parts of monosodium phosphate (anhydrous), two (2) parts of potassium ferricyanide, twenty-five (25) parts of sodium dichromate (hydrous), and thirty-three (33) parts of sodium sulphate (anhydrous). After dry mixing these quantities thoroughly they were added to the water to be tested so that there were 12 to 16 parts per million dichromate, 16 to 20 parts per million of PO_4 ion, 1.0 to 1.3 parts per million ferricyanide and a pH of between 5.5 and 7.5. Where herein and hereafter we employ the language "parts per million" or "p.p.m." we intend the same to have its recognized meaning in this art, namely milligrams per liter.

The water employed was Chicago, Illinois, tap water having an average partial composition as follows:

Ion:	P.p.m.
Calcium	30
Magnesium	10
Chloride	8
Sulphate	17

pH 8.2.

The water, after adding the corrosion inhibitor, was adjusted to a pH of 6.5 with sulphuric acid. The sulphate content of the water is raised by an average of about 45 parts per million by employing sulphuric acid to adjust the pH. Depending upon the parts per million concentration of the corrosion inhibitor the following test results were obtained:

Inhibitor, p.p.m.	Penetration in. per yr.	Percent [1] Inh.	Inhibitor, p.p.m.	Penetration, in. per yr.	Percent [1] Inh.
None	0.00750		70	0.00063	91.6
15	0.00209	72.2	85	0.00061	91.9
30	0.00134	82.2	100	0.00059	92.2
50	0.00074	90.2			

[1] Percentage of inhibition.

This test indicated that not over 50 parts per million of the inhibitor would be required to give satisfactory inhibition with Chicago tap water.

EXAMPLE II

In order to determine the optimum pH at which to operate a cooling system in which the inhibitor is employed another series of tests was performed with Chicago tap water adjusted to various values of pH with sulphuric acid. Throughout this series of tests the concentration of the inhibitor was held at a residual of 50 parts per million. The results were as follows:

Inhibitor residual 50 p.p.m.

pH of water:	Penetration in. per yr.
3.0	0.09086
4.0	0.00344
5.0	0.00196
6.0	0.00092
7.0	[1] 0.00073
8.0	[2] 0.00062

[1] Trace of scale detectable at 100 dia. magnification.
[2] Very light deposit of scale visible to naked eye.

From the foregoing two examples and other tests which have been performed the following conclusions may be drawn:

(1) A concentration of 50 p.p.m. of the inhibitor is sufficient for good inhibition at pH values between 5.0 and 8.0.

(2) Results obtained at pH 6.0 and 7.0 indicate that the optimum for good protection lies between these values, but effective inhibition results both below and above the pH range of 6.0 to 7.0.

EXAMPLE III

In order to illustrate the synergistic effect the various components of the mixture given in Example I have upon each other when used for the inhibition of corrosion, the following results were obtained in the laboratory. In all tests Chicago tap water adjusted to pH 6.5 with sulphuric acid was circulated in the apparatus already described in Example I, and control was the same, but only one, or a pair of the components of the mixture were used as the corrosion inhibitor. Results expressed as "penetration, inches per year" are compared with those obtained in the test cited in Example I.

TEST A

[Inhibitor—Sodium dichromate ($Na_2Cr_2O_7.2H_2O$)—Commercial.]

Results of Test		Results from Example I	
Inhibitor, p.p.m.	Penetration, in. per yr.	Inhibitor, p.p.m.	Penetration, in. per year
300	0.00127	30	0.00134
400	0.00067	50	0.00074

This test indicates that, weight for weight, and under the same conditions, the composition given in Example I is at least eight times as efficient as sodium dichromate (hydrous) when used alone.

TEST B

[Inhibitor—Commercial glassy sodium polyphosphate (anhydrous) essentially $Na_{12}P_{10}O_{31}$, approx. 85% PO_4.]

Results of Test		Results from Example I	
Inhibitor p.p.m.	Penetration, in. per yr.	Inhibitor, p.p.m.	Penetration, in. per yr.
50	0.00369 (very many small pits)	50	0.00074 (pitting absent)

This test indicates that, under the same conditions, the composition given in Example I is more than five times as effective as the polyphosphate alone, weight for weight, since it also prevents pitting.

TEST C

[Inhibitor—A mixture consisting of 90 parts glassy sodium polyphosphate (anhydrous) essentially $Na_{12}P_{10}O_{31}$, approx. 85% PO_4, and 10 parts potassium ferricyanide, $K_3Fe(CN)_6$.]

Result of Test		Result Test B, Ex. III		Results from Ex. I	
Inhibitor, p.p.m.	Penetration, in. per yr.	Inhibitor, p.p.m.	Penetration, in. per yr.	Inhibitor, p.p.m.	Penetration, in. per yr.
50	0.00137 (few small pits)	50	0.00369 (very many small pits)	50	0.00074 (pitting absent)

This test indicates that, under the same conditions, a mixture of 90% glassy polyphosphate and 10% potassium ferricyanide is more efficient, weight for weight, than the phosphate when used alone, but is much less efficient than the mixture used in Example I and moreover, does not prevent pitting.

EXAMPLE IV

In order to determine the effectiveness of the inhibitor in water having a high mineral concentration a series of tests was run at pH 6.5 on a synthetic water made up from Chicago tap water having the following partial analysis:

Ion:	P.p.m.
Calcium	925
Magnesium	200
Chloride	3800
Sulphate	2200

pH 8.2.

When this water was adjusted to pH 6.5 with sulphuric acid the sulphate content was raised to about 2650 p.p.m. In the corrosion test with this water, the pH was held at 6.5 which the foregoing examples indicated to be within the optimum range, and the concentration of the inhibitor was varied. The results obtained were as follows:

Inhibitor, p.p.m.	Penetration, in. per yr.	Percent Inhibition
None	0.00646	
15	0.00198	69.4
30	0.00072	88.8
50	0.00037	94.3
75	0.00032	95.1

No scale deposition could be detected on any of the coupons at 100 diameters magnification, indicating that

a pH of 6.5 is sufficiently low to prevent deposition in this highly mineralized water.

EXAMPLE V

In order to determine the inhibiting properties of this material in the presence of high chloride but otherwise low mineral content, another series was run in Chicago tap water containing various concentrations of chloride, the desired chloride concentration being obtained by the addition of sodium chloride. Tests were run at pH 6.5 with a concentration of 50 p.p.m. of inhibitor throughout the series. Results are tabulated below.

Chloride, p.p.m.	Penetration Without Inhibitor, in. per yr.	Penetration With Inh., in. per year	Percent Inhibition Calculated
500	0.01253	0.00110	91.0
1,000	0.01353	0.00101	92.5
4,000	0.01458	0.00098	93.3
9,000	0.01454	0.00111	92.4
14,000	0.01535	0.00127	91.7
20,000	0.01606	0.00154	90.4

When these results are compared with those obtained in Example II, it becomes readily apparent that the inhibitor is exceptionally effective on high sodium chloride solutions. All of the above results are well below the maximum commercially acceptable figure of 0.00500 inch per year (IPY). Furthermore, the resulting inhibition is uniform within the limits of experimental accuracy throughout the chloride concentration range. This result was unexpected, and not predictable from other experimental data relating to inhibitors exemplary of the invention.

EXAMPLE VI

In the petroleum industry where rigid requirements obtain for a corrosion inhibitor, the following formula gave excellent results:

	Parts
Disodium phosphate (anhydrous)	26
Monosodium phosphate (anhydrous)	18
Sodium dichromate	24
Sodium ferrocyanide	2
Sodium sulphate	30

The foregoing was controlled to 50 p.p.m. at a pH of 6 to 6.5.

In this industry the upper limit of satisfactory performance of a corrosion inhibitor is a corrosion rate of 0.005 IPY. In actual use in cooling towers at an operating refinery over a period of 90 days the average penetration rate was 0.0011 IPY as determined by 19 test coupons at various locations therein, or about one fifth the acceptable limit. The maximum rate was 0.0020 IPY and the minimum penetration rate shown was 0.0004 IPY.

From the foregoing examples and conclusions reached as well as many other tests which have been performed, the following conclusions as to the efficacy of, and treatment with, the inhibitor may be drawn:

(1) The inhibitor is highly effective within a pH range of 5.0 to 8.0 (optimum about 6.5) and somewhat beyond these values.
(2) In water low in chloride, sulphate and mineral content (such as Chicago tap water) a residual of between 40 and 60 p.p.m. (optimum about 50 p.p.m.) provides excellent inhibition.
(3) If the water to be treated is high in chloride content 50 to 60 p.p.m. of the inhibitor will also give excellent corrosion inhibition.
(4) If the water to be treated is high in both chloride and other mineral matter, a residual of 50 p.p.m. of the inhibitor will give as good or better inhibition than it does in a water low in these constituents.

Other examples of preparations which have exhibited highly effective corrosion inhibition are:

	Parts
Sodium ferrocyanide	4
Glassy polyphosphate	10
Sodium dichromate	60
Sodium sulphate (anhydrous)	26
	100

	Parts
Sodium polyphosphate	25
Sodium ferrocyanide	20
Sodium dichromate	15
Soda ash	40
	100

	Parts
Monosodium phosphate	20
Disodium phosphate	40
Sodium dichromate	33
Sodium ferrocyanide	3
Sodium sulphate	4
	100

	Parts
Disodium phosphate	8
Caustic potash [1]	6
Sodium ferrocyanide	14
Sodium dichromate	10
Water	62
	100

	Parts
Monosodium phosphate	13
Potassium ferricyanide	5
Sodium dichromate	15
Water	67
	100

[1] NOTE.—The caustic potash aids in the preparation of the product.

Some of the ortho-phosphates employed satisfactorily are disodium phosphate, tri-sodium phosphate, sodium-potassium phosphate, ammonium phosphates, and other soluble ortho-phosphates.

Monosodium phosphate has been found satisfactory in application when used to the exclusion of disodium phosphate. It has been observed, however, that by including the disodium phosphate additional corrosion preventive action takes place. In view of this observation, the ratio between the monosodium and disodium phosphates does not appear to be critical, but it has been observed that when the disodium phosphates are approximately twice the weight of the monosodium phosphates, excellent results are achieved.

Polyphosphates such as hexametaphosphate, tripolyphosphate, pyrophosphates and the glassy polyphosphates commercially available have proved equally satisfactory as the other phosphates. No water soluble phosphates have been found unsatisfactory for application in the inhibitor.

Many complex cyanides have been employed in the inhibitor, commercial sodium ferrocyanide having been found to give excellent results with easy control and low cost as additional advantages. Other complex cyanides which may be employed are soluble ferricyanides, nitroferricyanides and also organic nitriles.

Among others, the chromates which have been found to perform satisfactorily in the inhibitor are chromic acid, sodium dichromate (bichromate), potassium dichromate (bichromate) and other water soluble chromate compounds such as those of calcium and magnesium. No water soluble chromic acid compounds were found unsatisfactory.

The ratios of the various constituents of the inhibitor can vary considerably with relationship to each other as well as the total weight of the inhibitor, just as the total

weight of the inhibitor may vary with respect to the amount of water being treated. Also, it has been found that inert materials such as sodium sulphate or soda ash may be employed with the inhibitor to prevent any caking or cohesion of the mixed dry ingredients in transit when prepared in that form.

The foregoing tests described, as well as additional ones performed, indicate that although the various elements of the inhibitor employed alone will have certain very limited corrosion-inhibiting action, their combined corrosion protection at elevated temperatures far exceeds their individual or paired effect. This discovery of the combined corrosive inhibiting action of these various compositions could not have been predicted from the general knowledge in this field of chemistry, and particularly their advantageous and economic use under varying field conditions.

Although one particular embodiment of the invention has been shown and described in full here, there is no intention to thereby limit the invention to the details of such embodiment. On the contrary, the intention is to cover all modifications, alternative embodiments, usages and equivalents of the corrosion inhibitor as fall within the spirit and scope of the invention, specification and appended claims.

We claim as our invention:

1. A corrosion inhibiting composition consisting essentially of a water-soluble inorganic polyphosphate, a water-soluble inorganic complex cyanide, and a water-soluble inorganic chromate, said ingredients being present in parts, by weight, as follows:

	Parts
Water-soluble inorganic polyphosphate	8 to 40
Water-soluble inorganic complex cyanide	2 to 25
Water-soluble inorganic chromate	10 to 65

2. A corrosion inhibiting composition consisting essentially of a water-soluble inorganic phosphate, a water-soluble inorganic complex cyanide, and a water-soluble inorganic chromate, said ingredients being present in parts, by weight, as follows:

	Parts
Water-soluble inorganic phosphate	8 to 40
Water-soluble inorganic complex cyanide	2 to 25
Water-soluble inorganic chromate	10 to 65

3. A corrosion inhibiting composition consisting essentially of a water-soluble inorganic orthophosphate, a water-soluble inorganic complex cyanide, and a water-soluble inorganic chromate, said ingredients being present in parts, by weight, as follows:

	Parts
Water-soluble inorganic orthophosphate	8 to 40
Water-soluble inorganic complex cyanide	2 to 25
Water-soluble inorganic dichromate	10 to 65

4. A corrosion inhibiting composition consisting essentially of the following in the stated parts by weight:

	Parts
Monosodium phosphate	10 to 40
Sodium dichromate	25 to 65
Potassium ferricyanide	2 to 25

5. A corrosion inhibiting composition consisting essentially of the following ingredients in substantially the following parts by weight:

	Parts
Disodium phosphate	26
Monosodium phosphate	18
Sodium dichromate	24
Sodium ferrocyanide	2

6. A corrosion inhibiting composition consisting essentially of 40 parts anhydrous monosodium phosphate, 25 parts hydrous sodium dichromate, and 2 parts sodium ferrocyanide, said parts being by weight.

References Cited in the file of this patent

UNITED STATES PATENTS

Re. 23,740	Ryznar	Nov. 17, 1953
2,215,814	Hall	Sept. 23, 1940
2,248,656	Bird	July 8, 1941
2,728,652	Hance	Dec. 27, 1955