United States Patent Office

3,024,201
Patented Mar. 6, 1962

3,024,201

CORROSION INHIBITING COMPOSITION AND METHOD

Jacob I. Bregman, Park Forest, Ill., assignor to Nalco Chemical Company, a corporation of Delaware

No Drawing. Filed June 4, 1956, Ser. No. 589,018
10 Claims. (Cl. 252—387)

This invention relates to new and improved corrosion inhibiting compositions and to a new and improved method of inhibiting corrosion. The invention is particularly concerned with corrosion inhibiting compositions for preventing or inhibiting underwater corrosion in systems where water is moving, as through condensers, engine jackets, spray or cooling towers and distribution systems. The invention is especially valuable in inhibiting corrosion of ferrous metals, including iron and steel, and also in inhibiting the corrosion of non-ferrous metals, such as copper and admiralty metal (yellow brass containing about 1% tin).

It is known that various types of chromates have been used as corrosion inhibitors. Certain types of phosphates have also been employed for this purpose and combinations of phosphates and chromates have been used.

One of the objects of the present invention is to provide a new and improved chromium containing inhibitor which is more effective than chromate type inhibitors previously proposed.

Another object is to provide a new and improved synergistic composition of chemical components which produces new and improved results in preventing corrosion, especially in cooling tower systems such as the systems employed in conjunction with catalytic petroleum cracking units. Other objects will appear hereinafter.

In accomplishing these objects in accordance with the invention it has been found that new and improved results in preventing or inhibiting corrosion in ferrous and non-ferrous metals in contact with a corrosive medium containing water are obtained by dissolving in the corrosive medium a composition containing a soluble hexavalent chromium compound and a soluble hexavalent molybdenum or tungsten compound, and preferably also a compound capable of producing in aqueous solution a heavy metal cation from the group consisting of zinc, cobalt, nickel, mercury and trivalent chromium. These heavy metals are preferably employed as their water soluble salts or bases. They can also be used in the form of oil soluble ionizable salts where the corrosive medium is oily or contains an oil.

Especially advantageous results in the practice of the invention have been obtained by the employment of compounds which liberate a zinc ion in aqueous solution. Excellent results have also been obtained by the employment of compounds which liberate a nickel or cobalt ion in aqueous solution. The use of zinc compounds is preferred, however, particularly from the economic standpoint.

The compositions of the invention are preferably prepared in the form of solid compositions containing the active essential components. The following general formula is given to illustrate compositions which represent the best mode contemplated for the practice of the invention. In this formula it will be understood that ingredients A and B are essential components of the compositions of the invention. Ingredient C is an optional

but highly desirable additional component which very substantially improves the corrosion inhibiting effect of compositions composed of ingredients A and B. The weight ratios of A and B remain the same regardless of whether they are used in conjunction with ingredient C.

GENERAL FORMULA

Ingredients—	Percent by weight
(A) Ionizable hexavalent chromium compound, expressed as sodium dichromate ($Na_2Cr_2O_7.2H_2O$):	
(1) General range	50–98
(2) Preferred range	55–95
(3) Optimum range	60–75
(B) Ionizable hexavalent molybdenum or tungsten compound, expressed as sodium molybdate ($Na_2MoO_4.2H_2O$):	
(1) General range	2–15
(2) Preferred range	4–15
(3) Optimum range	4–12
(C) Heavy metal ion, expressed as $ZnSO_4.H_2O$:	
(1) General range	3–40
(2) Preferred range	8–30
(3) Optimum range	10–25

In the foregoing general formula the weight ratios of A:B:C may be varied between 1:(0.02–0.3):(0.033–0.80).

The following composition illustrates a preferred specific formula for the practice of the invention:

SPECIFIC FORMULA

Composition A:

Ingredients—	Percent by weight
Sodium dichromate ($Na_2Cr_2O_7.2H_2O$)	64.7
Sodium molybate (Na_2MoO_4)	6
Glassy sodium polyphosphate (containing 35.9% Na_2O and 64.1% P_2O_5 by weight)	3.6
Zinc sulfate ($ZnSO_4.H_2O$)	20.4
Sodium acid sulfate ($NaHSO_4$)	5.3

In the above specific formula the polyphosphate and the sodium acid sulfate are optional ingredients. The polyphosphate is added for the purpose of stabilizing calcium carbonate which may be present in the water to be treated. If calcium carbonate does not present a problem in the water to be treated the polyphosphate is omitted. However, since its presence does not adversely affect the use of the composition in any case it is preferable to incorporate it into the corrosion inhibiting composition in an amount such that the treated water will contain from 0.5 to 2 p.p.m. (parts per million), expressed as PO_4, of a polyphosphate and preferably about 1 p.p.m.

In order to adjust the pH of the system being treated it is sometimes desirable to include in the solid corrosion inhibiting composition a substance which will alter the normal pH of the composition. Thus, concentrated solutions of the corrosion inhibiting compositions containing 1% to 5% by weight of the active essential ingredients can be made by incorporating in the normally solid corrosion inhibiting compositions an acid compound such

as sodium hydrogen sulfate ($NaHSO_4$) or sulfamic acid (NH_2SO_3H), so as to produce a pH of 3.5 to 5 in the resulting solution.

The quantity of the corrosion inhibiting composition added to a liquid to inhibit corrosion of metals thereby is subject to variation but in general the range is from 3 to 75 parts (calculated as CrO_4) of the corrosion inhibiting composition per million parts by weight of the liquid being treated. A preferred range is around 5 to 50 p.p.m. of the composition, calculated on the basis of the CrO_4 therein, and an optimum range in most cases is 10 to 40 p.p.m. of the composition, calculated on the basis of the CrO_4 therein. The pH of the liquid being treated is preferably within the range of 5.5–8.5 and, in order to mitigate scale, a pH within the range from 6.5 to 7.5 is preferred.

The invention will be illustrated but is not limited by the following examples in which the quantities are stated in parts by weight unless otherwise indicated.

Example I

A composition of the previously described specific formula was added to a cooling tower water having the following analysis:

Ingredients:	Parts per million
Total dissolved solids (as $CaCO_3$)	1700
Chloride (as NaCl)	300
Calcium (as $CaCO_3$)	650
Silica (as SiO_2)	24
Magnesium (as $CaCO_3$)	600
Sulfate (SO_4) (as Na_2SO_4)	1300

This water was pumped through the tower and the cold water had a temperature around 60° F. The increase in temperature during the cooling operation was about 10° F. Steel test coupons were placed at the discharge end of the pump through which the water was pumped into the tower and also in the return line to the pump. A dosage of 20 p.p.m. of composition A previously described, calculated as CrO_4, was initially added to the cooling water. After the first week the test coupons showed a corrosion rate of 2.3 m.p.y. (mils per year) at the pump discharge. At the end of the second week the test coupons at the pump discharge showed an average corrosion rate of 1.6 m.p.y., at the end of the third week 1.3 m.p.y., and at the end of the fourth week 1.0 m.p.y. The corrosion rate at the pump return was 2.5 m.p.y. at the end of the first week, 1.7 m.p.y. at the end of the second week, 1.4 m.p.y. at the end of the third week, and 0.9 m.p.y. at the end of the fourth week.

For the sake of comparison, a comparable test was run with 10 p.p.m. of a composition consisting essentially of 29% of the glassy sodium polyphosphate of composition A, the remainder being sulfonated lignin, tannin, dextrine, sodium hydroxide and water and 40 to 60 p.p.m., expressed as CrO_4, of a commercial chromate type inhibitor containing 30% anhydrous sodium chromate, 30% anhydrous sodium dichromate and the remainder borax, sodium nitrate, dextrine and water. At the end of the first week the corrosion rate with these two combined compositions was approximately twice the corrosion rate with the composition of the present invention at both the pump discharge and the pump return. Even after four weeks the corrosion rate with the combined commercial formulas was still higher than the corrosion rate with composition A of the present invention at the pump discharge and more than twice as high at the pump return. Thus, composition A of the present invention was more effective at dosages containing ⅓ to ½ as much CrO_4 than the commercial chromate type composition.

The following examples are given to illustrate the corrosion inhibiting effects under varying test conditions with various combinations of ingredients.

The test apparatus used in the following examples consisted of a 2.5 liter vessel fitted with a cover adapted to hold the coupons which were of cold rolled mild steel (SAE 1020). The test water, unless otherwise stated, had the following composition:

Ingredients:	Parts per million
Total hardness (as $CaCO_3$)	400
Calcium hardness (as $CaCO_3$)	250
Magnesium hardness (as $CaCO_3$)	150
Chloride (as NaCl)	500
Sulfate (as Na_2SO_4)	1400

Throughout the test cycle the water was continuously aerated and stirred. At frequent intervals small volumes of the test water were removed and automatically replaced with fresh make-up. The rate of flow was about 10 liters per day, corresponding to a four-fold replacement of the contents. The pH was adjusted to the desired value in the test vessel by adding either sodium hydroxide or sulfuric acid. The temperature of the test water was maintained at about 150° F.

Example II

The first step was to determine the corrosion inhibition of sodium chromate at a pH of 7.0–7.5. The following results were obtained:

TABLE I

Test No.	Doasge p.p.m. as CrO_4	Corrosion rate (m.p.y.) after following number of days				
		1	2	3	7	15
1	0.0 (blank)	86.7	72.0	65.8	------	49.5
2	0.7	67.6	53.2	57.8	------	------
3	2.2	56.0	39.3	35.1	------	------
4	3.6	47.0	32.4	30.8	------	------
5	7.2	28.8	20.7	15.5	------	------
6	10.0	14.2	11.5	9.6	------	------
7	15.0	12.2	10.0	8.0	4.9	3.5

Various additional ingredients were then added to sodium chromate in the test waters under the same conditions with the following results, the concentration of sodium chromate, expressed as CrO_4, the test waters being 10 p.p.m.:

TABLE II

Test No.	Additive	Dosage p.p.m.	Corrosion rate (m.p.y.) after following number of days		
			1	2	3
8	No additive (except 10 p.p.m. CrO_4).	------	14.2	11.5	9.6
9	$NaBO_3$	50	25.6	21.7	15.1
10	Sodium ferrocyanide	50	18.0	12.5	8.3
11	do	25	19.0	12.8	8.1
12	NaF	50	17.9	16.2	10.2
13	Sodium persulfate	1	14.6	------	10.8
14	do	5	16.9	10.6	------
15	Sodium benzoate	25	18.7	------	------
16	35% by weight silica sol	100	19.2	11.3	8.4
17	$NaNO_2$	100	13.5	10.6	------
18	Na_2MoO_4, expressed as MoO_4.	1	11.4	9.6	6.9

It will be observed from Table II that the addition of the sodium molybdate gave a very pronounced improvement in the corrosion rate after three days even though only 1 p.p.m. of the sodium molybdate, as MoO_4, was added to the test water containing 10 p.p.m. of CrO_4. The use of 5 p.p.m. of the sodium molybdate as MoO_4, under the same conditions did not appear to substantially improve the corrosion inhibiting effect.

In a third series of tests corrosion inhibition was determined on steel test coupons and the standard test water under the same pH conditions of 7.0–7.5 with compositions containing a chromate and a molybdate as the essential components with or without the addition of the

polyphosphate of composition A with the following results:

TABLE III

Test No.	Chromate p.p.m. as CrO_4	Polyphosphate, p.p.m. as PO_4	Molybdate, p.p.m. as MoO_4	Corrosion rate (m.p.y.) after following number of days					
				1	2	3	5	7	10
19	3		0.75			26.3	12.1	9.8	
20	5		0.5			20.0	10.5	8.8	
21	7.5		0.75	18.1					
22	10		0.1					5.5	5.0
23	10		0.5					6.1	5.3
24	10		1.0	11.4	9.6	6.9		4.8	
25	10		3.0	10.2	7.2	4.9			
26	10		5.0	11.9	7.7				
27	15		1.5	10.2					
28	15	1.0	1.5	10.8				4.7	2.9

It will be observed again that excellent results were obtained by using a combination of a chromate and a molybdate. In the last composition in the table which also contained 1 p.p.m. of a polyphosphate very good results were obtained. However, from other tests it did not appear that there was any noticeable effect on the corrosion rate due to the presence of the polyphosphate.

Tests were then run with the standard test water containing various additional components using as the corrosion inhibiting composition the last composition in Table III which had the following formula:

Composition B:

Ingredients—	Percent by weight
Sodium dichromate dihydrate	84.8
Sodium polyphosphate shown in composition A	5.2
Sodium molybdate dihydrate	10.0

These tests were made (A) at a pH of 7.0–7.5 with the standard test water to which had been added various additional components and (B) at varying pH's with the results shown in the following table:

TABLE IV

A

Test No.	Condition varied	Corrosion rate (m.p.y.) after following number of days		
		1	2	7
29	Add 150 p.p.m. SiO_2 (sodium metasilicate) to test water.	9.2		4.7
30	Reduce SO_4 in test water to 1,000 p.p.m.	7.5		2.6
31	Reduce total hardness [1] in test water to 200 p.p.m.	9.2		3.1

B

32	pH of 6.0–6.5	14.1	10.9	
33	pH of 6.5–7.0	12.6	10.0	
34	pH of 7.5–8.0	10.4	8.3	

[1] Same Ca:Mg ratio as in standard test water.

The addition of SiO_2 to the test water appeared to give a slight reduction in one day corrosion results but made no difference after seven days. The reduction of the SO_4 and the total hardness contents both appeared to have improved corrosion inhibition. The tests with various pH variations indicated that in the range of pH 6–8 the effectiveness of this composition was definitely increased with increasing pH.

Example III

The next step was to add a small amount of zinc to Composition B tested as previously described in connection with the test results given in Table III. When two p.p.m. of zinc (5.5 p.p.m. $ZnSO_4.H_2O$) was added to the water and tested at a pH of 7.0 to 7.5 on the standard test water under the test conditions previously noted a pronounced improvement in corrosion inhibition was obtained not only on ferrous metals but also on copper and on admiralty metal as shown by the following test results:

TABLE V

Test No.	Composition	Corrosion rate (m.p.y.)					
		1 day			4 days		
		Fe	Cu	Admiralty	Fe	Cu	Admiralty
35	Composition B	10.4	2.6	2.3	8.2	1.8	1.6
36	Composition B + 2 p.p.m. Zn (Added as $ZnSO_4.H_2O$).	5.3	2.9	2.5	2.2	1.1	0.8
37	No Inhibitor	95.7	8.1	8.4	46.6	4.3	6.4

A series of tests was then run with various combinations on the standard test water at a pH of 7.0 to 7.5 under the standard test conditions previously described with the results shown in the following table:

TABLE VI

Test No.	Chromate as CrO_4 p.p.m.	Molybdate as MoO_4, p.p.m.	Polyphosphate as PO_4, p.p.m.	Zinc as Zn p.p.m.	Corrosion rate (m.p.y.) after—		
					1 day	7 days	13 days
38	15	1.5	1.0	0.25	10.7		
39	15	1.5	1.0	0.50	7.2	3.0	2.3
40	15	1.5	1.0	1.0	5.2	3.0	2.3
41	15	1.5	1.0	2.0	5.9	2.4	1.8
42	15	1.5	1.0	3.0	6.7		
43	15	1.5	1.0	5.0	6.3		
44	15			2.0	11.9		
45	15	1.5		2.0	6.5		
46	15		1.0	2.0	9.7		
47	15	1.0	1.0	2.0	5.8		
48	15	2.0	1.0	2.0	5.5		
49	10	1.5	1.0	2.0	9.3		
50	15	0.5	1.0	2.0	7.0		
51	15	0.75	1.0	2.0	7.2		
52	15	1.25	1.0	2.0	7.5		
53	15	1.5	1.0	1.5	5.2		

It will be observed in the foregoing table that in test 44 the additive composition contained 15 p.p.m. of CrO_4 and 2 p.p.m. of zinc without the molybdate and the resultant corrosion rate was relatively high as compared with the rate in test 45 where the molybdate was present.

Example IV

Tests were then made to determine the effect of adding 2 p.p.m. of metals other than zinc to the composition used in tests 28 to 34 and the following results were observed with the standard test water at a pH of 7.0 to 7.5 under the test conditions previously described.

TABLE VII

Test No.	Metal	Corrosion Rate (m.p.y.) after—		
		1 day	7 days	15 days
54	Composition B (blank)	10.8	4.7	
55	Cadmium ($CdCl_2$)	12.4		
56	Manganese ($MnSO_4$)	13.3		
57	Lead ($Pb(NO_3)_2$)	17.1		
58	Copper ($CuSO_4$)	12.8		
59	Cobalt ($CoSO_4$)	4.8	2.5	1.6
60	Nickel ($NiSO_4$)	5.2	1.7	1.7
61	Mercury ($HgCl_2$)	8.5	3.3	2.4
62	Chromium ($CrCl_3$)	6.6	2.7	1.8

It will be observed from the results of the foregoing tests that the cadmium, manganese, lead and copper salts all gave results showing no improvement over composition B whereas the cobalt, nickel, mercuric and chromic salts all produced a substantial improvement in corrosion inhibition as compared with composition B.

Example V

When a composition such as that used in test 36, supra, is employed a rather difficultly soluble material results due to the reaction of the zinc compounds with the chromate and/or molybdate in the formula. It was found that this could be overcome by adding a minor amount, preferably about 5% of sodium bisulfate. This also made the pH of a concentrated solution sufficiently acid to permit the ready preparation of a 5% solution of the corrosion inhibiting composition in water. The addition of the bisulfate did not appear to affect the corrosion inhibition as shown by the following test results at a pH of 7 to 7.5 on the standard test water under the standard conditions previously given:

TABLE VIII

Test No.	Composition	Composition dosage p.p.m.	Chromate as CrO_4 p.p.m.	Corrosion Rates (m.p.y.) after—		
				1 day	7 days	15 days
63	C	34.6	15	7.2	2.0	1.3
64	D	29.1	15	7.3	2.2	1.6
65	E	41.0	15	6.4	2.1	1.7
66	F	32.8	15	6.8	2.1	1.6

In Table VIII the composition, C, D, E and F contain the following ingredients:

Ingredients	C	D	E	F
$Na_2Cr_2O_7.2H_2O$	58.5		8.5	61.6
Na_2CrO_4			38.9	
$K_2Cr_2O_7$		65.3		
Na_2MoO_4 (anhydrous, technical grade)	5.9	6.7	4.7	6.2
Sodium polyphosphate of composition A	3.6	4.0	2.8	3.8
$ZnSO_4.7H_2O$	27.0		21.6	28.4
$ZnSO_4.H_2O$		19.0		
Na_2SO_4			10.0	
$NaHSO_4$	5.0	5.0	13.5	

The results in Table VIII show that the sulfate and bisulfate additions have no substantial effect on the corrosion inhibiting properties of the compositions of the invention.

Example VI

Tests were then made on a number of different waters using composition A at various dosages with the following results:

TABLE IX

Test No.	Dosage, p.p.m.	Chromate as CrO_4, p.p.m.	Test water	Corrosion rate (m.p.y.) after following number of days					
				1	2	3	7	10	15
67	29.3	15.0	Standard water	7.8		4.5	2.7	2.0	1.4
68	29.3	15.0	A	6.6			1.4		
69	19.6	10.0	A	10.0			1.5		
70	9.6	5.0	A	19.0		9.6			
71	29.3	15.0	C	4.5	3.1				
72	19.6	10.0	C	8.2		4.2			
73	9.8	5.0	C	25.2					
74	29.3	15.0	B	10.7		4.3			
75	29.1	15.0	D	7.6					

In the foregoing test waters the compositions of the waters were as follows:

Water	Parts per Million			
	A	B	C	D
Total hardness as $CaCO_3$	1,250	1,400	840	138
Calcium as $CaCO_3$	650	800	640	110
Magnesium as $CaCO_3$	600	600	250	28
Chloride as NaCl	275	263	275	210
SO_4 as Na_2SO_4	1,310	1,490	1,404	325

These waters simulate actual waters at several locations in the United States.

Example VII

Tests were made using a composition consisting of sodium chromate and the sodium polyphosphate of composition A on the standard test water under the standard test conditions with the results given in Table X:

TABLE X

Test No.	Chromate as CrO_4, p.p.m.	Polyphosphate as PO_4, p.p.m.	pH	Corrosion rate (m.p.y.) after—			
				1 day	2 days	3 days	5 days
76	15	20	6.5–7	11.3	8.6	------	2.4
77	10	13.3	6.5–7	15.5	10.8	------	------
78	7.5	10.0	6.5–7	18.5	12.4	------	------
79	10	20.0	6 –6.5	15.4	11.9	8.5	------
80	5	10	6 –6.5	21.3	------	------	------

It will be observed that the test results with the chromate and phosphate alone are inferior to those obtained with the water using a composition of the present invention as shown by test 27 in Table III and test 45 in Table VI. The pH ranges shown above are those which are used with these chromate-polyphosphate compositions in actual practice. They are chosen so as to minimize phosphate sludge formation.

It will be recognized that the invention is susceptible to some variation and modification in the manner of its practical application. It is generally desirable to employ the anionic ingredients of the corrosion inhibiting composition in the form of their alkali metal salts, e.g., sodium and potassium. It will be understood, however, that such ingredients can be employed in the form of other water soluble compounds. For example, the CrO_4 ion can be supplied as ammonium chromate or dischromate or chromic acid. The molybdenum and tungsten compounds can be supplied as their ammonium salts or as the acids.

Other compositions within the scope of the invention may be afforded by using the several heavy metal ions herein described in the form of cations of either the hexavalent chromium, molybdenum and tungsten compounds. Thus, zinc chromate, dichromate, molybdate and tungstate may be employed. In addition to the zinc salts such compounds as nickel molybdate, chromic molybdate, mercuric molybdate, nickel chromate, chromic tugnstate, and nickel tungstate may be used. The necessary solubility can be achieved by proper pH control. The amount of heavy metal ion necessary to afford synergistic activity would, of course, remain within the ranges specified. By using these compounds the heavy metal salts may be omitted as a separate component of the several preferred formulations herein shown.

If a polyphosphate is employed as a part of the corrosion inhibiting composition or added separately to the liquid being treated in order to stabilize water against scale or incrustation any of the ionizable water soluble to difficultly soluble polyphosphate compounds can be used in accordance with the practice set forth in Fink and Richardson, U.S. 2,358,222 in amounts up to about 9 parts per million parts by weight of aqueous solution. Examples of polyphosphates which are suitable for this purpose are any one or more of the following: sodium acid pyrophosphate, tetrasodium pyrophosphate, sodium tripolyphosphate ($Na_5P_3O_{10}$), sodium tetraphosphate ($Na_4P_6O_{13}$), calcium acid pyrophosphate, sodium trithiotetraphosphate ($Na_6P_4O_{10}S_3$), any of the water soluble polyphosphate glasses or so-called molecularly dehydrated phosphates in which the ratio of Na_2O to P_2O_5 may be variable, including those known as "sodium hexametaphosphate" and "glassy septaphosphate," as well

as complexes containing calcium and sodium, magnesium and sodium and aluminum and sodium.

The invention is especially valuable in inhibiting corrosion of ferrous metals, as well as certain non-ferrous metals such as copper and admiralty metal by adding the compositions of the invention to the corrosive medium. Exceptionally good results have been obtained in inhibiting corrosion in cooling towers and other distribution systems in which water is moving. The corrosion inhibiting composition may be prepared in the form of a liquid concentrate prior to its addition to the corrosive medium and added by means of a proportioning pump or in any other suitable manner. It is usually preferable to add the corrosion inhibiting composition in an amount such that it is more than adequate to prevent corrosions initially and then to reduce the amount until the optimum results are obtained at a minimum dosage. One procedure, for example, is to add composition A to cooling tower water at a dosage of 20 p.p.m. (as CrO_4) and then reduce the dosage to 10 p.p.m. The quantity of molybdate or tungstate ion employed in conjunction with the chromate is normally sufficient to improve the corrosion inhibition as compared with the chromate alone at the same dosage. The quantity of other heavy metal ions such as zinc, cobalt, nickel, mercury and/or trivalent chromium is normally sufficient to enhance corrosion inhibition of the corrosion inhibiting composition as a whole when compared with the results obtained with the combined use of the hexavalent chromium and hexavalent molybdenum and/or tungsten ions.

The invention is hereby claimed as follows:

1. A corrosion inhibiting composition consisting essentially of (A) 50 to 98 weight percent, calculated as $Na_2Cr_2O_7.2H_2O$, of an ionizable hexavalent chromium compound, (B) 2 to 15 weight percent, calculated as $Na_2MoO_4.2H_2O$, of an ionizable compound from the group consisting of hexavalent molybdenum and hexavalent tungsten compounds and (C) 3 to 40 weight percent, calculated as $ZnSO_4.H_2O$, of an ionizable compound from the group consisting of zinc, cobalt, nickel, mercury and trivalent chromium compounds, the weight ratio of A:B:C being within the range of 1:0.02–0.3:0.033–0.80.

2. A corrosion inhibiting composition consisting essentially of (A) 55 to 95 weight percent, calculated as $Na_2Cr_2O_7.2H_2O$, of an ionizable hexavalent chromium compound, (B) 4 to 15 weight percent, calculated as $Na_2MoO_4.2H_2O$, of an ionizable compound from the group consisting of hexavalent molybdenum and hexavalent tungsten compounds, and (C) 8 to 30 weight percent, calculated as $ZnSO_4.H_2O$, of an ionizable compound from the group consisting of zinc, cobalt, nickel, mercury and trivalent chromium compounds, the weight ratio of A:B:C being within the range of

1:(0.02–0.3):(0.033–0.80)

3. A corrosion inhibiting composition consisting essentially of (A) 60 to 75 weight percent, calculated as $Na_2Cr_2O_7.2H_2O$, of an ionizable hexavalent chromium compound, (B) 4 to 12 weight percent, calculated as $Na_2MoO_4.2H_2O$, of an ionizable compound from the group consisting of hexavalent molybdenum and hexavalent tungsten compounds, and (C) 10 to 25 weight percent, calculated as $ZnSO_4.H_2O$, of an ionizable compound from the group consisting of zinc, cobalt, nickel, mercury and trivalent chromium compounds, the weight ratio of A:B:C being within the general range of 1:(0.02–0.3):(0.033–0.80).

4. A corrosion inhibiting composition consisting essentially of the following:

Ingredients—	Percent by weight
Sodium dichromate (calculated as $Na_2Cr_2O_7.2H_2O$)	60–75
Sodium molybdate (calculated as $Na_2MoO_4.2H_2O$)	4–12
Zinc sulfate (calculated as $ZnSO_4.H_2O$)	10–25

and containing a sufficient amount of sodium acid sulfate to prevent the formation of insoluble zinc compounds in a 5 percent by weight aqueous solution of said composition.

5. A process of inhibiting the corrosion of metals in contact with a corrosive medium containing water which comprises dissolving in said medium a corrosion inhibiting composition consisting essentially of (A) 50 to 98 weight percent, calculated as $Na_2Cr_2O_7.2H_2O$, of an ionizable hexavalent chromium compound and (B) 2 to 15 weight percent, calculated as $Na_2MoO_4.2H_2O$, of an ionizable compound from the group consisting of hexavalent molybdenum and hexavalent tungsten compounds, the weight ratio of (A) to (B) being within the range from 1:0.02 to 1:0.3

6. A process of inhibiting the corrosion of metals in contact with a corrosive medium containing water which comprises dissolving in said medium a corrosion inhibiting composition consisting essentially of (A) 50 to 98 weight percent, calculated as $Na_2Cr_2O_7.2H_2O$, of an ionizable hexavalent chromium compound, (B) 2 to 15 weight percent, calculated as $Na_2MoO_4.2H_2O$, of an ionizable compound from the group consisting of hexavalent molybdenum and hexavalent tungsten compounds and (C) 3 to 40 weight percent, calculated as $ZnSO_4.H_2O$, of an ionizable compound of a metal from the group consisting of zinc, cobalt, nickel, mercury and trivalent chromium, the weight ratio of A:B:C being within the range of 1:(0.02–0.3):(0.033–0.80).

7. A process of inhibiting the corrosion of metals in contact with a corrosive medium containing water which comprises dissolving in said medium a corrosion inhibiting composition consisting essentially of (A) 55 to 95 weight percent, calculated as $Na_2Cr_2O_7.2H_2O$, of an ionizable hexavalent chromium compound, (B) 4 to 15 weight percent, calculated as $Na_2MoO_4.2H_2O$, of an ionizable compound from the group consisting of hexavalent molybdenum and hexavalent tungsten compounds, and (C) 8 to 30 weight percent, calculated as $ZnSO_4.H_2O$, of an ionizable compound of a metal from the group consisting of zinc, cobalt, nickel, mercury and trivalent chromium, the weight ratio of A:B:C being within the range of 1:(0.02–0.3):(0.033–0.80).

8. A process of inhibiting the corrosion of metals in contact with a corrosive medium containing water which comprises dissolving in said medium a corrosion inhibiting composition comsisting essentially of (A) 60 to 75 weight percent, calculated as $Na_2Cr_2O_7.2H_2O$, of an ionizable hexavalent chromium compound, (B) 4 to 12 weight percent, calculated as $Na_2MoO_4.2H_2O$, of an ionizable compound from the group consisting of hexavalent molybdenum and hexavalent tungsten compounds, and (C) 10 to 25 weight percent, calculated as $ZnSO_4.H_2O$, of an ionizable compound of a metal from the group consisting of zinc, cobalt, nickel, mercury and trivalent chromium, the weight ratio of A:B:C being within the general range of 1:(0.02–0.3):(0.033–0.80).

9. A process of inhibiting the corrosion of ferrous metals in contact with a corrosive medium containing water which comprises dissolving in said medium a corrosion inhibiting composition consisting essentially of the following:

Ingredients—	Percent by weight
Sodium dichromate (calculated as $Na_2Cr_2O_7.2H_2O$)	60–75
Sodium molybdate (calculated as $Na_2MoO_4.2H_2O$)	5–12
Zinc sulfate (calculated as $ZnSO_4.H_2O$)	10–25

and containing a sufficient amount of sodium acid sulfate to prevent the formation of insoluble zinc compounds in

a 5 percent by weight aqueous solution of said composition, and a sufficient amount of an ionizable polyphosphate to produce a PO_4 content in water of 0.5 to 9 p.p.m., said composition being added to water in proportions of 3 to 75 p.p.m. calculated as CrO_4.

10. A process of inhibiting the corrosion of ferrous metals in contact with a corrosive medium containing water which consists essentially of dissolving in said medium 5 to 50 p.p.m., calculated as CrO_4, of (A) an ionizable hexavalent chromium compound, (B) a quantity of an ionizable compound from the group consisting of hexavalent molybdenum and hexavalent tungsten compounds, and (C) a quantity of an ionizable compound of a metal from the group consisting of zinc, cobalt, nickel, mercury and trivalent chromium, the weight ratio of (A), calculated as $Na_2Cr_2O_7.2H_2O$, to (B), calculated as $Na_2MoO_4.2H_2O$, to (C), calculated as $ZnSO_4.H_2O$, being within the range of 1:(0.0.02–0.3):(0.0.80), and the pH being within the range of 5.5 to 8.5.

References Cited in the file of this patent

UNITED STATES PATENTS

1,565,043	Avis	Dec. 8, 1925
2,147,409	Lamprey	Feb. 14, 1939
2,358,222	Fink et al.	Sept. 12, 1944
2,695,876	Fariss	Nov. 30, 1954
2,711,391	Kahler	June 21, 1955
2,755,170	Stubblefield	July 17, 1956
2,872,281	Kahler et al.	Feb. 3, 1959
2,900,222	Kahler et al.	Aug. 18, 1959

FOREIGN PATENTS

736,215	Great Britain	Sept. 7, 1955

OTHER REFERENCES

Robertson: Molybdate and Tungstate as Corrosion Inhibitors and the Mechanism of Inhibition, article in Jour. of the Electro-chemical Society, March 1951, vol. 98, No. 3, pages 94 to 100.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,024,201 March 6, 1962

Jacob I. Bregman

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, TABLE I, in the heading to column 2 thereof, for "Doasge" read -- Dosage --; column 6, TABLE VI, columns 7 and 8, line 2 thereof, strike out "3.0" and "2.3", respectively; column 8, line 39, for "dischromate" read -- dichromate --; line 49, for "tugnstate" read -- tungstate --; column 11, line 18, for "1:(0.0.02-0.3):(0.0.80)" read -- 1:(0.02-0.3):(0.033-0.80) --.

Signed and sealed this 24th day of July 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,024,201 March 6, 1962

Jacob I. Bregman

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 4, TABLE I, in the heading to column 2 thereof, for "Doasge" read -- Dosage --; column 6, TABLE VI, columns 7 and 8, line 2 thereof, strike out "3.0" and "2.3", respectively; column 8, line 39, for "dischromate" read -- dichromate --; line 49, for "tugnstate" read -- tungstate --; column 11, line 18, for "1:(0.0.02-0.3):(0.0.80)" read -- 1:(0.02-0.3):(0.033-0.80) --.

Signed and sealed this 24th day of July 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents