

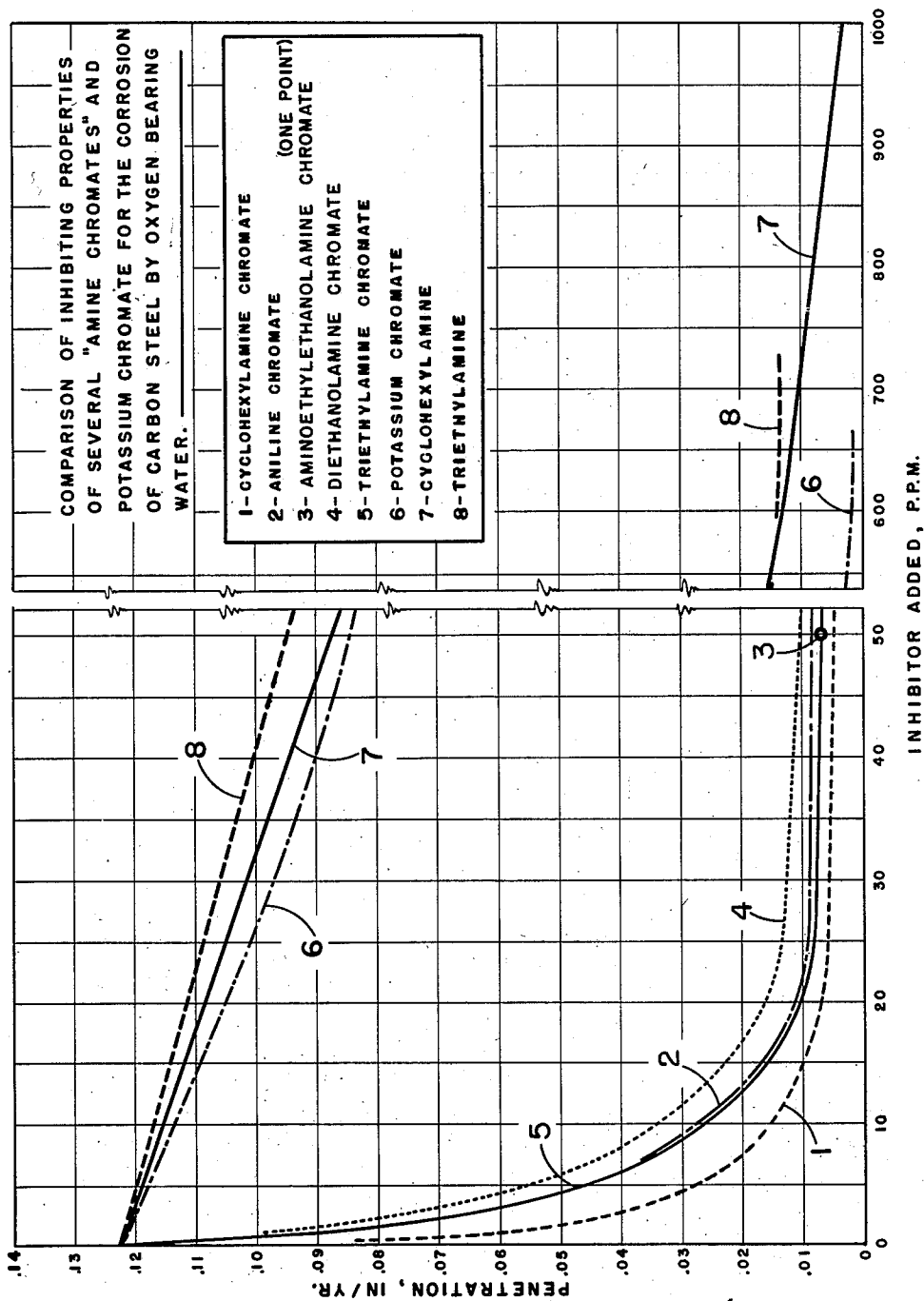
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CORROSION INHIBITION

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CORROSION INHIBITION

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The present invention is directed to a composition and a method for preparing same. More particularly the invention is directed to a composition suitable for use as a corrosion inhibitor and a method for preparing the composition. In its more particular aspects, the invention is directed to a new chromium salt, a method of preparing same and the employment of the composition in inhibiting the corrosivity of corrosive solutions to ferrous metal surfaces.

Prior to the present invention it has been known to employ alkali metal chromium salts as corrosion inhibitors to inhibit the corrosivity of oxygen bearing water. It has also been known to inject alkali metal salts of chromium into wells producing corrosive fluids from subsurface formations. For example, it has been known to use potassium and sodium chromate as corrosion inhibitors in oxygen bearing water and also as corrosion inhibitors in wells producing gas and liquid from subsurface formations such as oil and gas wells. It has been common heretofore to introduce the potassium and sodium chromates into water or into well fluids and the like to inhibit the corrosivity of the corrosive fluids against ferrous metal surfaces such as vessels and metal conduits with which they come into contact. Oxygen is known to be present in water used in industrial processes such as petroleum refining and such water is quite corrosive to ferrous metal surfaces with which it comes into contact such as in condenser boxes and the like. The corrosive media in well fluids such as those in the type referred to is usually hydrogen sulfide or carbon dioxide, which may be produced in substantial quantities, depending on the locale of the well.

It has also been known to employ various amines such as cyclohexylamine as corrosion inhibitors in steam systems. Berk, in the U. S. Bureau of Mines publication "Observations on the Use of Cyclohexylamine in Steam," discusses the use of amines and particularly cyclohexylamine as a corrosion inhibitor in systems where corrosion is due to the presence of carbon dioxide. Chamberlain has disclosed in U. S. 1,719,649 and U. S. 1,719,650, the employment of amines as corrosion inhibitors in acidic solutions. Other patentees such as Hitch in U. S. 1,206,220, Gann et al. in U. S. 1,992,205 and Saukaitis in U. S. 2,049,517 have disclosed the inhibiting action of sodium and potassium chromates, sodium bichromate and the inhibiting power of various amines in inhibiting the corrosivity of acidic media to various alloys. Thus from the foregoing discussion of the prior art it will be seen that it

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is old to employ amines or chromates as corrosion inhibitors.

The corrosion inhibitors of the prior art, either amines or chromates, have the one great disadvantage in requiring appreciable amounts of the inhibitors to passivate the corrosivity of various solutions to which they may be added. In other words, substantial quantities of the compounds of the prior art have been necessary. These corrosion inhibitors are quite costly and besides, in industrial systems, add other ingredients to the corrosive solution which may be disadvantageous.

It is, therefore, the main object of the present invention to provide an improved composition adapted for use as a corrosion inhibitor of corrosion to ferrous metals due to aqueous solutions containing oxygen, hydrogen sulfide and carbon dioxide.

Another object of the present invention is to provide a method for preparing a composition adapted for use as a corrosion inhibitor in corrosive aqueous solutions containing oxygen, hydrogen sulfide or carbon dioxide in contact with ferrous metal surfaces.

It is another object of the present invention to provide an improved method for inhibiting the corrosivity of aqueous solutions in contact with ferrous metal surfaces.

A still further object of the present invention is to provide a method for inhibiting the corrosivity of aqueous solutions containing corrosive amounts of oxygen, hydrogen sulfide and carbon dioxide in contact with a ferrous metal surface.

The objects of the present invention may be achieved by preparing a composition adapted to be used as a corrosion inhibitor, as described, by reacting a solution of an acidic chromium compound and an amine.

The objects of the present invention may also be achieved by maintaining in the corrosive solution in contact with ferrous metal surfaces containing oxygen, hydrogen sulfide or carbon dioxide, a small but effective amount of the reaction product of an acidic chromium compound and an amine.

Thus, the present invention may be briefly described as involving a composition comprising a reaction product of an acidic chromium compound and an amine.

The invention also involves preparing a composition by forming an aqueous solution of an acidic chromium compound such as the chromic acids, salts of polychromic acids, and acid chromium salts and adding to the aqueous solution

thereof at substantially atmospheric temperatures a quantity of an amine such that one mole of amine is present to react with every acid chromate ion originally present or subsequently produced by hydrolysis of the chromium compounds to form a reaction product.

The present invention further involves maintaining in a corrosive solution containing oxygen, hydrogen sulfide, and/or carbon dioxide in contact with the ferrous metal surface a small but effective amount of the reaction product of an amine and an acidic chromium compound, such as the chromic acids, the salts of polychromic acids and acid chromium salts in the range between 5 and 500 parts per million of the corrosive solution.

The term "acidic chromium compound" refers to those compounds which when placed in aqueous solution will have a pH less than 7. Examples of such salts are potassium dichromate, sodium acid chromate, potassium trichromate, and sodium trichromate. It is to be noted that an alkali metal chromate such as potassium chromate or sodium chromate will not react with amines in accordance with this invention since they form solutions with a pH greater than 7. It is well known, however, that in acid solution the chromates tend to form polychromates, the concentration of which depends upon the pH of the solution and the concentration of the salt. These polychromates will react with amines in accordance with the present invention as described hereinafter.

In preparing the improved composition, an acidic chromium compound of the type illustrated such as an alkali metal dichromate, is dissolved in water to the extent of forming a solution which is only partially saturated. It is desirable to employ the highest practical degree of concentration of the acidic chromium compound solution, but care should be exercised in preparing the solution since, if the solution is too concentrated, it may cause oxidation to occur as will be described. A primary, secondary, or tertiary amine is then added to the aqueous solution of the acidic chromium salt. If the aqueous solution contains too much of the acidic chromium compound there is some danger of oxidation of the amine by the solution. The degree of saturation may be determined by the skilled workman. The amine is reacted with the aqueous solution of the chromium compound acid chromium salt until a pronounced color change takes place. With potassium dichromate the aqueous solution is a brilliant orange which on reaction with an amine changes to an intense yellow. When the reaction has been completed, as indicated by the color change, the reaction product has been formed which is suitable as a corrosion inhibitor and may be used as such as a solution or the reaction product may be recovered from the solution by evaporation of the solution to dryness to cause separation of the crystalline salts.

The temperatures employed are essentially room temperatures, that is, a temperature in the range from about 60 to 100° F. While the reaction is taking place some heat will be evolved as normally occurs in acid-alkali reactions. However, elevated temperatures should be avoided since oxidation of the amine by the acid chromium compound may occur. It is undesirable to use temperatures in excess of about 212° F.

While solutions of greater strength may be em-

ployed, satisfactory results have been obtained with solutions of potassium dichromate containing 10% by weight of the salt. The amount of the amine employed should be sufficient to provide at least two moles of amine for each mole of the acid chromium compound in the aqueous solution.

In general, one mole of amine will react with every mole of acid chromate present originally or formed in solution. For example, a mole of potassium dichromate, which hydrolyzes to form two moles of the acid chromate, requires two moles of amine to form the reaction product of the present invention. To illustrate this, 50 grams of potassium dichromate were placed into aqueous solution. The solution, which had a deep orange color, was titrated with cyclohexylamine until the color changed to yellow. This color change, which was quite pronounced, occurred when 39 cc. of the cyclohexylamine had been added. The 50 grams of potassium dichromate corresponds to 0.17 mole whereas the 39 cc. of cyclohexylamine corresponds to 0.32 mole. Thus, within the limits of experimental error, 2 moles of the amine were required for one mole of the dichromate. Since any of the salts of the polychromic acids hydrolyze to form the acid chromate, they may be used to form the amine chromates. For the trichromate, 3 moles of the amine would be required, for the tetrachromate, 4 moles of the amine would be required, etc.

It has been stated that the chromium compound to be used with the present invention must form an aqueous solution with a pH less than 7. Any of the compounds illustrated, such as the chromic acids, salts of polychromic acids, or acid chromium salts, meet this criterion. Alkali metal chromates on the other hand form solutions whose pH is greater than 7 and, thus, will not react in accordance with the present invention. This is illustrated by the following example: 20 grams of sodium chromate were added to 200 cc. of distilled water and the pH was found to be 9. Two drops of cyclohexylamine were added to this solution whereupon the pH immediately rose to a value of slightly greater than 11, thus indicating that the cyclohexylamine was not reacting with the chromate. For the purpose of comparison, three drops of cyclohexylamine were added to 200 milliliters of distilled water and the pH was found to be 11.

It is well known that the chromates, if placed in a strong enough acid solution, tend to form the polychromates. The concentration of the polychromates formed depends upon the pH of the solution and the concentration of the chromate originally present. The polychromates formed in such a manner will react with amines in accordance with the present invention. For convenience, however, it is preferred to use either the chromic acids or the salts of the polychromic acids, or an acid chromium salt since solutions of these compounds do not have to be adjusted for pH in order to obtain the reaction product. The preferred compound is potassium dichromate since it is readily soluble, readily available, and at the present time one of the less expensive sources of the desired acid chromate ion.

The reaction product is thermally stable at an evaporation temperature of 212° F.

In order to illustrate the present invention further, reaction products in accordance with the present invention were formed by reacting at room temperature two primary amines, cyclohexylamine and aniline, a secondary amine, di-

ethanolamine, a tertiary amine, tri-ethylamine, and a mixed primary-secondary amine, amino-ethylethanolamine, with potassium dichromate in accordance with the procedure set out before. Reaction products were formed which, for convenience in description, will be termed cyclohexylamine chromate, aniline chromate, amino-ethylethanolamine chromate, diethanolamine chromate and tri-ethylamine chromate, but it is to be clearly understood that I do not wish to limit myself by such terminology since the exact structural composition of the reaction product is not understood.

The reaction products of the several amines and potassium dichromate were then added to oxygen saturated surface water (from the San Jacinto River, Harris County, Texas) in varying amounts in a laboratory scale circulating water system in which the velocity and temperature of the water simulated those of a normal plant cooling system actually employing this river water. Weighed specimens of carbon steel were exposed in this system at two different velocities (0.124 and 1.575 feet per second) of this water into which air was continuously bubbled. The difference in corrosion rate of these specimens under the influence of the various inhibitors was determined by conventional laboratory techniques.

These results are compared in Table I which presents the amount of the various inhibitors added to the oxygen bearing water, the corrosion rate and penetration in inches per year as evidenced by the weight loss of the specimens of carbon steel after contact with the corrosive solution and the per cent of reduction.

TABLE I

Corrosion of carbon steel by oxygen-bearing water

Inhibitor Added	Amount, p. p. m.	Corrosion rate, in./yr.	Percent Reduction
None.....		0.122	
Cyclohexylamine.....	100	0.0727	40.5
Do.....	200	0.0471	61.5
Do.....	1,000	0.0035	97.1
Triethylamine.....	300	0.0253	79.2
Do.....	700	0.0144	88.2
Potassium chromate.....	100	0.0603	50.7
Do.....	300	0.0139	88.6
Do.....	600	0.0030	97.5
Cyclohexylamine chromate.....	10	0.0148	87.9
Do.....	50	0.0030	97.5
Do.....	100	0.0062	94.9
Aniline chromate.....	25	0.0091	92.5
Do.....	100	0.0073	94.0
Aminoethylethanolamine chromate.....	50	0.0068	93.4
Diethanolamine chromate.....	25	0.0130	89.3
Do.....	100	0.0046	96.2
Tri-ethylamine chromate.....	25	0.0078	93.6
Do.....	100	0.0037	97.0

The data in the foregoing table have been plotted in the single figure of the drawing to illustrate more clearly the advantages of the present invention over that of the prior art. From the data presented it is obvious that as little as 10 parts per million of the cyclohexyl amine chromate is as effective an inhibitor as almost 300 parts per million of potassium dichromate or between 500 and 600 parts per million of cyclohexyl amine. This is particularly significant since it is known that introduction of too low a concentration of an inhibitor such as potassium chromate will actually increase the corrosion as shown by U. R. Evans in his article "Use of soluble inhibitors, fundamental principles," Industrial and Engineering Chemistry, 37:703, 1945.

The data further illustrate that the tertiary amine, triethyl amine, when reacted with potassium dichromate has this same synergistic inhibiting effect because a concentration of about 10 parts per million of this reaction product is as effective as about 300 parts per million of chromate or 600 to 700 parts per million of the amine. Calculation of the concentration of a mixture of either of these amines and potassium chromate that must be used to give at least as good inhibition as either one alone, would indicate the use of a total concentration not significantly lower than that of either compound in its purest state. For example, to reduce the penetration to 0.03 inch per year, the data presented, which are plotted in the drawing, would indicate the necessity of using a concentration of about 200 parts per million of potassium chromate or about 250 parts per million of triethylamine, or possibly a mixture of about 100 parts per million of potassium chromate and about 125 parts per million of triethylamine. Instead of this, a concentration of less than 10 parts per million of the reaction product prepared in accordance with the present invention may be used. Thus, the unexpected inhibiting properties of this reaction product allow much lower concentrations of inhibitor to be used with the same or superior effects to that obtained with much higher concentrations of potassium chromate or amine alone. A comparison of the inhibiting properties of several of the amine chromates prepared in accordance with this invention with that of potassium chromate under the same conditions is also given in the drawing.

Water was then saturated with carbon dioxide at atmospheric pressure and room temperature of 85° F. The pH of the saturated solution was 5.2. Portions of the water were then tested for corrosivity to specimens of carbon steel, while other portions had added to it potassium chromate, cyclohexylamine and the reaction product of cyclohexylamine and potassium di-chromate in varying quantities using the circulating system previously described. The specimens of carbon steel were exposed to the corrosive action of the solution of carbon dioxide for identical lengths of time, withdrawn and weighed to determine the metal loss. The following table gives the concentration of the inhibitor in the carbon dioxide solution, the corrosion rate measured in penetration of the metal in inches per year and the per cent of reduction as shown by the several inhibitors.

TABLE II

Corrosion of carbon steel by water saturated with carbon dioxide¹

Inhibitor Added	Amount, p. p. m.	Corrosion rate, in./yr.	Percent Reduction
None.....		0.210	
Potassium chromate.....	100	0.0178	91.5
Do.....	500	0.0108	94.9
Do.....	1,000	0.0064	96.9
Cyclohexylamine.....	1,000	0.080	62.0
Cyclohexylamine chromate.....	10	0.0115	94.5
Do.....	25	0.0005	99.8

¹ Saturated with carbon dioxide at atmospheric pressure and room temperature (85° F.). pH of saturated solution is 5.2.

It will be immediately apparent from the foregoing data that 100, 500 and 1000 p. p. m. of potassium chromate added to the corrosive solution of carbon dioxide resulted in reduction of

corrosion of 91.5%, 94.9% and 96.9%, respectively. It will also be apparent that 1000 p. p. m. of cyclohexylamine reduces the corrosion of the carbon steel by 62.0%. On the other hand, it will be quite apparent that the reaction product of the present invention in amounts of 10 and 25 p. p. m. reduced the corrosion by 94.5% and 99.8%, which may be compared with the 500 and 1000 p. p. m. of potassium chromate and 1000 p. p. m. of cyclohexylamine.

Water was then saturated with hydrogen sulfide at atmospheric pressure and room temperature of 85° F. The hydrogen sulfide saturated water was then divided into several portions for testing in the circulating system previously described. One portion was tested to determine its corrosivity to specimens of carbon steel, while another portion had added to it 1000 p. p. m. of potassium chromate. Two other portions had added to them, respectively, 100 and 500 p. p. m. of the reaction product of cyclohexylamine and potassium dichromate. Specimens of carbon steel were suspended in the several portions of the hydrogen sulfide saturated water and the corrosivity of the solutions determined to the specimens of carbon steel suspended therein after a specified length of time. The amount of corrosion was measured by weighing the specimens after withdrawing them from the corrosive solution. The results of these tests are given in Table III, which shows the amount of the inhibitor

of cyclohexylamine and potassium dichromate as with 1000 p. p. m. of potassium chromate.

Additional runs were then made in which specimens of Admiralty metal, which is a copper bearing alloy having the following approximate composition:

29% zinc
70% copper
1% tin

10 Plus a trace (about .03%) of arsenic to prevent dezincification,

was suspended in a 10% solution of ammonium hydroxide and a 10% solution of sodium hydroxide in water. The corrosivity of the solutions to the Admiralty metal without inhibitor and with inhibitor was determined. In one instance the inhibitor was potassium chromate and in another instance it was the reaction product of pyridine and potassium di-chromate. The effect of this inhibitor was compared with the inhibition effect of potassium chromate. With respect to the sodium hydroxide solution, the corrosivity of the solution without an inhibitor and with the reaction product of cyclohexylamine and potassium dichromate was determined.

These results are given in Table IV in which the amount of inhibitor added and corrosion rate in penetration in inches per year and per cent of reduction due to the presence of the inhibitor are given.

TABLE IV

Corrosion of copper bearing alloys in alkaline solutions

Solution	Metal	Inhibitor Added	Corrosion rate, in./yr.	Percent Reduction
10% NH ₄ OH solution ¹	Admiralty	None	0.022	
Do.	do.	5,000 p. p. m. potassium chromate	0.009	59.0
Do.	do.	5,000 p. p. m. Pyridine	0.011	50.0
Do.	do.	5,000 p. p. m. Pyridine chromate	0.013	41.0
10% NaOH solution ²	do.	None	0.0395	
Do.	do.	500 p. p. m. Cyclohexylamine chromate.	0.0267	32.4

¹ Static solution in a beaker at room temperature (85° F.).

² Tests made in laboratory circulating system described before.

added, the corrosion rate measured in penetration in inches per year and the per cent of reduction.

TABLE III

Corrosion of carbon steel by water saturated with hydrogen sulfide ¹

Inhibitor Added	Amount, p. p. m.	Corrosion rate, in./yr.	Percent Reduction
None		0.0835	
Potassium chromate	1,000	0.0100	88.0
Cyclohexylamine chromate	100	0.0195	76.6
Do.	500	0.0100	88.0

¹ Saturated at atmospheric pressure and room temperature (85° F.).

It will be seen from the data in Table III that potassium chromate in the amount of 1000 p. p. m. reduced the corrosivity of the solution by 88.0%, whereas the reaction product of cyclohexylamine and potassium dichromate in amounts of 100 and 500 p. p. m. reduced the corrosivity of the solution by 76.6% and 88.0% respectively, the same percentage of reduction in corrosivity being obtained with 500 p. p. m. of the reaction product

It will be apparent from the data in Table IV that 5000 p. p. m. of potassium chromate reduces the corrosivity to Admiralty metal by 59%, whereas the same quantity of pyridine reduces it by 50.0%. It will also be apparent that the reaction product of pyridine and potassium dichromate reduces the corrosivity by only 41.0%, while 500 p. p. m. of the reaction product of cyclohexylamine and potassium dichromate reduces the corrosivity of the sodium hydroxide solution to Admiralty metal by 32.4%.

The corrosivity of acid solutions to specimens of carbon steel was then determined. The acid solutions were solutions of hydrochloric acid, sulfuric and acetic acids. A 10% hydrochloric solution had added to it potassium chromate, pyridine and the reaction product of pyridine and potassium dichromate. A 40% sulfuric acid solution had added to it potassium chromate, pyridine and the reaction product of pyridine and potassium dichromate while a 10% acetic acid solution had added to it the reaction product of cyclohexylamine and potassium dichromate. The specimens of carbon steel were suspended in the various acidic solutions at room temperature of 85° F. under static conditions. After exposing the specimens to the corrosive solution for various lengths

of time, the specimens were withdrawn and weighed to determine the loss in metal. Table V, which follows, shows the inhibitor and amount added, corrosion rate in inches of penetration per year and the per cent reduction, if any, due to the various inhibitors.

TABLE V

Corrosion of carbon steel by acid solutions

Solution	Inhibitor Added	Corrosion rate, in./yr.	Percent Reduction
10% HCl Solution ¹	None	0.215	
Do	5,000 p. p. m. $K_2Cr_2O_7$	0.374	² 74.0
Do	5,000 p. p. m. Pyridine	0.152	29.4
Do	500 p. p. m. Pyridine Chromate	0.357	² 66.0
40% H_2SO_4 Solution ¹	None	1.845	
Do	5,000 p. p. m. $K_2Cr_2O_7$	4.52	² 145.0
Do	5,000 p. p. m. Pyridine	2.52	² 37.0
Do	5,000 Pyridine Chromate	4.54	² 146.0
10% Acetic Acid Solution	None	0.412	
Do	1,000 p. p. m. Cyclohexylamine Chromate	0.221	46.3

¹ Static solution in a beaker at room temperature (85° F.).

² Increased.

It will be seen from the data in Table V that both potassium dichromate and the reaction product of potassium dichromate and pyridine actually increased the corrosivity of hydrochloric acid to the specimens of carbon steel, while some reduction in corrosion was obtained with pyridine. Similarly, it may be seen that the potassium dichromate and the reaction product thereof with pyridine all increased the corrosivity of the 40% sulfuric acid solution to carbon steel, while the reaction product of cyclohexylamine and potassium dichromate in an amount of 1000 p. p. m. reduced the corrosivity of 10% acetic acid solution to carbon steel by 46.3%.

The present invention is susceptible to application to inhibition of any type of ferrous metal surfaces in contact with a corrosive solution containing oxygen, hydrogen sulfide or carbon dioxide. For example, in many industrial plants, including petroleum refineries, it is frequently necessary to use water in contact with various metallic equipment such as condensers, condenser boxes, heat exchangers and the like. Since this water contains oxygen, it is frequently very corrosive, resulting in loss to both equipment and operating efficiency.

The invention is also applicable to the storage and transportation of petroleum and its products, since entrained water settles out in pipe lines and tanks and this water containing oxygen, carbon dioxide, and/or hydrogen sulfide is usually the cause of corrosion of pipe lines with the attendant economic loss requiring shutdown of equipment and replacement thereof. It is, therefore, considered that the present invention has wide application to any operation in which ferrous metal alloys are exposed to the corrosive action of aqueous solutions containing oxygen, hydrogen sulfide and/or carbon dioxide.

The invention may also be applicable to the prevention of corrosion of steel tubing, well head equipment, and product lines experienced in some gas condensate wells producing sweet gas or condensate fluids by contact with connate water or entrained water which contains carbon dioxide and organic acids as the corrosive media.

The mechanism by which the reaction product of an acid chromium salt and an amine is effective in preventing corrosion of ferrous metals is not fully understood, but it is believed that the protection is based on an extremely thin, self-healing film formed by the interaction of the

reaction product of the amine and the salt with the ferrous metal surface. The characteristics and behavior of ferrous metals treated in accordance with the present invention in which they are contacted with an aqueous solution containing oxygen or carbon dioxide to which has been added

the reaction product of an amine and acid chromium salt bears a striking resemblance to the resistance of the ferrous alloy stainless steel to corrosion. It is believed that the activity of the iron surface may be passivated by the reaction product of the amine and the acid salt. In other words, the iron becomes more noble than prior to treatment and less susceptible to attack because the positive electrochemical potential of the iron surface is reduced. It is understood, of course, that I do not wish to bind myself to any theory offered as explanation of the beneficial effects of this invention.

While numerous examples of amines have been given, it is to be understood that I do not wish to limit myself thereto and that any primary, secondary, or tertiary amine may be used in reaction with any compound selected from the group of chromic acids, salts of polychromic acids, or acid chromium salts. Examples of some other primary amines that may be used with the present invention are butylamine, methylamine, propylamine, benzylamine, ethanolamine, and isoamylamine. Other secondary amines that may be used with the present invention are dibutylamine, dimethylamine, diphenylamine, methyl-ethanolamine, dimethanolamine, and dipropylamine. Additional tertiary amines that may be used with the present invention are tributylamine, trimethylamine, triethanolamine, methyl-di-ethylamine, and tripropylamine. Complex or mixed amines may also be used with the present invention. Some examples of these other than the aminoethylethanolamine used herein are melamine, diazine, and triazine (either the symmetrical or unsymmetrical isomers).

Also it is to be understood that while I have confined my description and examples to the alkali metal dichromates, such as illustrated by potassium dichromate, the other alkali metal dichromates such as the lithium and sodium dichromates may be used in lieu thereof although the potassium di-chromate forms a preferred reactant in the practice of my invention. It is also to be understood that while potassium dichromate has been employed as an illustration thereof, other salts may be used, such as for example lithium and sodium dichromates and other chromium salts may be used in lieu of potassium dichromate.

The nature and objects of the present invention having been fully described and illustrated, what

I wish to claim as new and useful and to secure by Letters Patent is:

1. A method for inhibiting the corrosivity of aqueous solutions containing corrosive amounts of a corrosive material selected from the class consisting of oxygen, hydrogen sulfide, carbon dioxide, and their mixtures in contact with a ferrous metal surface which comprises adding to said corrosive solution a small but effective amount of the reaction product resulting when an only partially saturated aqueous solution of an acidic chromium salt having a pH less than 7 has added thereto an amine selected from the group consisting of primary, secondary, tertiary and mixed amines at a temperature within the range of 60° to 100° F., the amine and the solution of acidic chromium salt being employed in amounts sufficient to provide equimolar amounts of amine and acidic chromium salt to form a homogeneous solution of said reaction product.

2. A method for inhibiting the corrosivity of aqueous solutions containing corrosive amounts of a corrosive material selected from the class consisting of oxygen, hydrogen sulfide, carbon dioxide, and their mixtures in contact with a ferrous metal surface which comprises adding to said corrosive solution prior to contact with said ferrous metal surface an amount of the reaction product resulting when an only partially saturated aqueous solution consisting of an acidic chromium salt having a pH less than 7 has added thereto an amine selected from the group consisting of primary, secondary, tertiary and mixed amines at a temperature within the range of 60° to 100° F., the amine and the solution of acidic chromium salt being employed in amounts

sufficient to provide equimolar amounts of amine and acidic chromium salt to form a homogeneous solution of said reaction product in the range from 5 to 500 parts per million of said corrosive solution.

3. A method for inhibiting the corrosivity of aqueous solutions containing corrosive amounts of a corrosive material selected from the class consisting of oxygen, hydrogen sulfide, carbon dioxide, and their mixtures in contact with a ferrous metal surface which comprises adding to said corrosive solution an amount of the reaction product resulting when an only partially saturated aqueous solution of potassium dichromate has added thereto an amine selected from the group consisting of primary, secondary, tertiary and mixed amines at a temperature within the range of 60° to 100° F., the amine and the solution of potassium dichromate being employed in amounts sufficient to provide equimolar amounts of amine and potassium dichromate to form a homogeneous solution of said reaction product in the range between 5 and 500 parts per million of said corrosive solution.

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