

[54]	INHIBITED TREATING ACID	3,507,795	4/1970	Gardner.....	252/147 X
[75]	Inventors: Bill R. Keeney; Joe W. Johnson, Jr., both of Duncan, Okla.	3,658,720	4/1972	McDougall et al.	252/148 X
		3,686,129	8/1972	Loucks	252/147
		3,705,106	12/1972	Muzyczko et al.....	134/3 X
[73]	Assignee: Halliburton Company, Duncan, Okla.	2,049,517	8/1936	Saukaitis.....	252/149 X
		3,249,547	5/1966	Fisher	21/2.7 X
[22]	Filed: Oct. 28, 1970	3,260,673	7/1966	Fisher	252/389 X
		2,559,580	7/1951	Alexander.....	252/389 X
[21]	Appl. No.: 86,978	2,377,966	6/1945	Reed.....	23/150
		2,567,156	9/1951	Malowan	252/389 X
[52]	U.S. Cl..... 21/2.7 R, 134/3, 134/41, 252/147, 252/148, 252/389	Primary Examiner—Barry S. Birchman			
[51]	Int. Cl. C23f 11/04, C23g 1/04, C23g 1/06	Attorney—John H. Tregoning			
[58]	Field of Search..... 21/2.5, 2.7; 252/389, 394, 147, 148; 134/3, 41, 42	[57] ABSTRACT			
[56]	References Cited	The present invention is directed to an inhibited treat-			
	UNITED STATES PATENTS	ing acid for use in contact with ferrous surfaces at			
3,146,208	8/1964	Fisher	252/148	temperatures of from about 150°F to about 450°F.	
3,243,379	3/1966	Clayton.....	252/148	17 Claims, No Drawings	
3,404,094	10/1968	Keeney	252/148		

INHIBITED TREATING ACID

The present invention relates generally to the field of protecting ferrous metals from the corrosive effects of acids, and has particular application in situations where the temperature at which the metal and acid are in contact is between about 150°F and 450°F.

Ferrous metals are sought to be protected from the corrosive effects of acids when, for example, acids are used to clean ferrous metal forms or when acids are passed through ferrous metal conduits enroute to treat another substance, such as the treatment of a subterranean formation with acid by passing the acid through an oil well casing enroute to the formation. Many various types of compositions have been used to reduce the corrosive effects of acids on ferrous metals. Nitrogen compositions and acetylenic compositions have been found to be useful in most cases to inhibit the corrosive effects of acids on ferrous metals. Typical acid corrosion inhibitors are those taught in U.S. Pat. Nos. 3,514,410, 3,404,094, 3,107,221 and 2,993,863. A particular failing of these acid corrosion inhibitors of the prior art is that their effectiveness is greatly reduced in the presence of temperatures greater than about 200°F.

Various metals and metal ions have been used in the past as acid corrosion inhibitors but with unsatisfactory results at temperatures greater than about 200°F. For example, copper has been added to the acid as cuprous oxide and as cuprous chloride. However, only limited improvement in corrosion inhibition at high temperatures has been noted. Arsenic has also been used as an acid corrosion inhibitor. However, it has been found that arsenic will not provide high temperature acid corrosion inhibition in acid strengths above about 17 percent by weight of acid in water. In addition, arsenic has been known to produce poisonous arsine gas when used as an acid corrosion inhibitor. When arsenic is used as an inhibitor in acid for treating oil wells, any arsenic which becomes mixed with oil produced from said well has been found to have an adverse effect on the catalysts used in refineries where the oil is processed.

Tin and iodine have been used as tin chloride and potassium iodide in efforts to intensify the effects of acid corrosion inhibitors. However, only limited success has been obtained.

The present invention provides an inhibited treating acid for use at temperatures of from about 150°F to about 450°F where acid corrosion to metals in contact with said inhibited treating acid is sought to be limited to not more than about 0.10 lbs./ft.², which comprises a treating acid selected from the group consisting of organic and inorganic acids and mixtures thereof, an acid corrosion inhibitor selected from the group consisting of nitrogen compounds, acetylenic compounds and mixtures thereof, and cuprous iodide present in a concentration of from about 25 ppm (parts per million) at temperatures of from about 150°F to about 25,000 ppm at temperatures of about 450°F.

In the preferred form of the invention cuprous iodide is combined with an acid which may be hydrochloric acid, sulfuric acid, hydrofluoric acid, acetic acid or mixtures thereof (hereinafter referred to as "treating acid"), and an acid corrosion inhibitor which may be an acetylenic compound, a nitrogen compound, or a mixture thereof (hereinafter referred to as "acid corrosion inhibitor") to produce a highly inhibited treating

acid which is especially useful at temperatures of from about 150°F to about 450°F.

Cuprous iodide is combined with the treating acid and acid corrosion inhibitor in amounts sufficient to prevent corrosion to ferrous metal surfaces from exceeding about 0.10 lbs./ft.² during any period of contact between the ferrous metal surface and the treating acid-acid corrosion inhibitor-cuprous iodide mixture (hereinafter referred to as "inhibited treating acid").

Cuprous iodide, when placed in solution, has a Cu⁺ to I⁻ ratio of about 1:2. That is about 2,000 ppm cuprous iodide placed in solution will yield about 668 ppm Cu⁺ ions and about 1,332 ppm I⁻ ions. Experimentation has disclosed that if exactly the above ratio of Cu⁺ ions and I⁻ ions are provided from soluble salts for an in situ formation of cuprous iodide, the degree of corrosion inhibition provided thereby is not as great as expected from cuprous iodide. However, it has been found that an excess of from about 5 percent to about 15 percent of the compound supplying the I⁻ ions will provide the desired degree of inhibition.

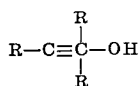
It has been discovered that the cuprous iodide produced in situ by reactants which also form free iodine will operate in the inventive manner, but show a smaller degree of improvement. Therefore, the most preferred reactants for producing cuprous iodide in situ are those which do not produce free iodine. Therefore, preferred compounds for forming cuprous iodide in situ (in the treating acid either before or after said acid is combined with said acid corrosion inhibitor) are acid soluble salts of iodine and acid soluble salts of copper which, upon reacting, do not form free iodine. Examples of such salts are potassium iodide and sodium iodide as a source of iodide ions and cuprous chloride and cuprous oxide as a source of copper ions. Examples of other salts which may be used as a source of copper ions are cupric chloride and cupric sulfate; however, these are not preferred salts because they form free iodine when reacted with iodine salts.

To be effective, the cuprous iodide must be combined with the treating acid-acid corrosion inhibitor mixture in concentrations of from about 25 ppm by weight of said mixture at temperatures of about 150°F to about 25,000 ppm by weight of said mixture at temperatures of about 450°F. The amount of cuprous iodide required to produce the desired degree of inhibition (less than about 0.10 lbs./ft.²) varies with the temperature of the intensified treating acid and with the efficiency of the acid corrosion inhibitor used. Most relatively inefficient acid corrosion inhibitors, when mixed with the treating acid, require about 25,000 ppm cuprous iodide at temperatures of about 450°F to prevent corrosion to ferrous surfaces in contact with said inhibited treating acid from exceeding 0.10 lbs./ft.². If less than about 25,000 ppm cuprous iodide is present at temperatures of about 450°F, the corrosion to ferrous metals in contact with the intensified treating acid will exceed 0.10 lbs./ft.². However, it is to be understood that smaller concentrations of cuprous iodide may be effective in preventing corrosion to ferrous surfaces from exceeding 0.10 lbs./ft.² at 450°F if a relatively more efficient acid corrosion inhibitor is combined with the treating acid. If less than 25 ppm cuprous iodide is combined with the treating acid and the acid corrosion inhibitor at about 150°F, no intensification of the acid corrosion inhibition of the treating acid-acid corrosion inhibitor mixture is noted.

The acid corrosion inhibitor to be combined with the treating acid and the cuprous iodide can be an acetylenic compound, a nitrogen compound or a mixture thereof. It may be an inhibitor taught in U.S. Pat. Nos. 3,514,410, 3,404,094, 3,107,221, 2,993,863 and 3,382,179.

Some examples of acetylenic compounds which may be employed in the present invention are hexynol, dimethyl hexynol, dimethyl hexynediol, dimethyl hexynediol, dimethyl octynediol, methyl butynol, methyl pentynol, ethynyl cyclohexanol, 2-ethyl hexanol, phenyl butynol, and ditertiary acetylenic glycol.

Other acetylenic compounds which can be employed in accordance with the present invention are for example, butynediol, 1-ethynylcyclohexanol, 3-methyl-1 nonyn-3-ol, 2-methyl-3-butyn-2-ol; also 1-propyn-3-ol, 1-butyn-3-ol, 1-pentyn-3-ol, 1-heptyn-3-ol, 1-octyn-3-ol, 1-nonyn-3-ol, 1-decyn-3-ol, 1-(2,4,6-trimethyl-3 cyclohexenyl)-3-propyne-1-ol, and in general acetylenic compounds having the general formula



wherein R is —H, alkyl, phenyl, substituted phenyl or hydroxy-alkyl radical, and the alpha R's may be joined together to form a cyclohexyl ring.

Acetylenic sulfides having the general formula



can also be employed in the present invention in lieu of acetylenic alcohols. Examples of these are dipropargyl sulfide, bis (1-methyl-2-propynyl) sulfide and bis (2-ethynyl-2-propyl sulfide).

The nitrogen or ammonia compounds that can be employed in accordance with the present invention are those amines such as mono, di and trialkyl amines having from two to six carbon atoms in each alkyl moiety as well as the six membered N-heterocyclic amines, for example, alkyl pyridines and mixtures thereof. This includes such amines as ethylamine, diethylamine, triethylamine, propylamine, dipropylamine, tripropylamine, mono, di and tributylamine, mono, di and tripropylamine, mono, di and trihexylamine and isomers of these such as isopropylamine, tertiarybutylamine, etc. This also includes alkyl pyridines having from one to five nuclear alkyl substituents per pyridine moiety, said alkyl substituents having from one to 12 carbon atoms and preferably those having an average of six carbon atoms per pyridine moiety, such as a mixture of high boiling tertiary-nitrogen - heterocyclic compounds such as HAP (High Alkyl Pyridines), Reilly 10-20 base and Alkyl Pyridines HB.

The acid corrosion inhibitor should be present in the inhibited treating acid in a concentration of from about 0.1 percent at temperatures of about 150°F to about 2.5 percent at temperatures of about 450°F by volume of inhibited treating acid. Acid corrosion inhibitor concentrations greater than about 2.5 percent by volume of inhibited treating acid do not produce an increase in acid corrosion inhibition at any temperature, and concentrations of acid corrosion inhibitor of less than 0.1 percent by volume of inhibited treating acid results in little or no acid corrosion inhibition at temperatures of about 150°F or greater.

Examples of commercially available acid corrosion inhibitors useful in the inhibited treating acid are HAI-50 and Blend-57 (Halliburton Services, Inc.), Dowell-A110 (Dow Chemical Co.), and Wellaid-211 (AMOCO brand).

The treating acid useful in the present invention may be hydrochloric acid, hydrofluoric acid, sulfuric acid and mixtures thereof. The acid should be present in strengths of from about pH 6.5 to about 35 percent by weight of acid in water. Acids weaker than those having a pH of 6.5 do not perform as treating acids, and those having an acid strength greater than 35 percent by weight of acid in water are too corrosive to be used as treating acids.

Corrosion loss to metal surfaces treated with acids is generally measured in pounds of metal taken into solution by the treating acid per square foot of metal surface exposed to said acid. An acid corrosion loss of about 0.05 lbs./ft.² is generally thought of as being an acceptable loss during an acid treatment, although slightly higher corrosion losses are sometimes considered acceptable at temperatures of about 400°F or greater, if the corrosion is uniform. Heretofore, metal surfaces could not generally be exposed to treating acids at temperatures above about 150°F without exceeding an acid corrosion loss of about 0.05 lbs./ft.². Corrosion losses in the presence of treating acids tend to rise with the temperature of said acid. Acid corrosion inhibitors used with the treating acids are not able to maintain acid corrosion losses within the above described acceptable limits at temperatures up to about 450°F.

For example, an API Type N-80 metal surface treated with 30 percent hydrochloric acid containing Blend-57 acid corrosion inhibitor in a concentration of about 2.0 percent by volume of the hydrochloric acid demonstrated a corrosion loss of about 0.77 lbs./ft.² after about two hours contact at about 300°F. between the treating acid-acid corrosion inhibitor mixture. This is well above the acceptable limit of 0.05 lbs./ft.². However, when the same concentrations of treating acid and acid corrosion inhibitor are combined with 11,000 ppm cuprous iodide to form the inhibited treating acid of the present invention, the acid corrosion loss experienced under the same contact conditions is about 0.04 lbs./ft.², safely within the acceptable acid corrosion limit.

Under the same conditions, except at a contact temperature of about 400°F and a treating acid strength of 15 percent, an API Type N-80 metal surface will dissolve when exposed to the treating acid-acid corrosion inhibitor mixture. However, when exposed to the inhibited treating acid of the present invention containing about 15,000 ppm cuprous iodide, the acid corrosion loss is held to about 0.062 lbs./ft.².

Experiments have also shown that corrosion can be significantly reduced by combining cuprous iodide with treating acid-acid corrosion inhibitor mixtures comprising an acid other than hydrochloric acid. For example, at 200°F with a contact time of 6 hours a 10 percent sulfuric acid-acid corrosion inhibitor mixture will produce a 0.07 lbs./ft.² corrosion loss on API Type N-80 metal. The addition of 500 ppm cuprous iodide to said treating acid will reduce the corrosion to 0.021 lbs./ft.². Under similar conditions the addition of 500 ppm cuprous iodide will reduce the corrosion caused by 10 percent acetic acid and an acid corrosion inhibi-

tor from about 0.0016 to about 0.0014 lbs./ft.². In similar mixtures, the addition of 500 ppm cuprous iodide reduces the corrosion caused by a 15% hydrochloric-10% acetic acid blend from about 0.010 to about 0.005 lbs./ft.²; a 12% hydrochloric-3% hydrofluoric blend from about 0.019 to about 0.004 lbs./ft.².

The effectiveness of weak acid corrosion inhibitors such as ethyl octynol can be dramatically improved by the addition of cuprous iodide. For example, a mixture containing 15 percent hydrochloric acid and ethyl octynol in a concentration of about 0.3 percent by weight of acid will produce a corrosion loss of about 0.38 lbs./ft.² to the surface of API Type N-80 metal during a contact time of 6 hours at 200°F. The addition of 500 ppm cuprous iodide, forming an inhibited treating acid, will reduce the corrosion to about 0.044 lbs./ft.².

Cuprous iodide has been found to produce an acceptable acid corrosion reduction when combined with treating acid-acid corrosion inhibitor mixtures at temperatures above about 150°F, where other compounds containing copper and iodine have not been effective. For example, in a mixture of acid corrosion inhibitor and 15 percent hydrochloric acid the addition of 7,000 ppm cuprous iodide prevented the acid corrosion from exceeding about 0.013 lbs./ft.² on API Type N-80 metal surface after a contact time of two hours at 350°F. The addition to the same mixture of 7,000 ppm ferrous iodide resulted in a corrosion loss of about 0.182 lbs./ft.²; the addition of iodopropane, about 0.236 lbs./ft.²; the addition of iodomethane, about 0.320 lbs./ft.²; the addition of cupric sulfide, about 0.226 lbs./ft.²; and the addition of cuprous sulfide, about 0.241 lbs./ft.². It is clear, then, that the combination of cuprous iodide with an acid corrosion inhibitor and a treating acid produces a surprising improvement in the protection of metal surfaces against acid corrosion.

It has also been discovered that cuprous iodide will operate as an acid corrosion inhibitor at temperatures of less than about 150°F. That is, cuprous iodide may be added to a treating acid or formed in situ in the treating acid at concentrations of from about 50 ppm to about 3,000 ppm to reduce acid corrosion to a metal surface in contact with the treating acid. If less than about 50 ppm cuprous iodide is combined with the treating acid, no significant decrease in acid corrosion is noted. If more than about 3,000 ppm cuprous iodide is added to the treating acid, no additional improvement in the acid corrosion inhibition is found.

For example, when API Type J-55 steel is exposed to 15 percent hydrochloric acid at a temperature of about 150°F for about two hours, a corrosion loss to the steel surface can be measured at about 0.037 lbs./ft.². However, when 250 ppm cuprous iodide is added to the treating acid the corrosion is reduced to about 0.012 lbs./ft.², and when 3,000 ppm cuprous iodide is added to the treating acid the corrosion is reduced to about 0.007 lbs./ft.².

The inhibited treating acid herein described may be used to treat subterranean formations having a temperature of between about 150°F and about 450°F while preventing corrosion to the casing or tubing used to transmit the inhibited treating acid to said formations from exceeding about 0.10 lbs./ft.². In such an acid treatment of said subterranean formations, especially of oil or gas wells, the inhibited treating acid may be mixed in any sequence. That is, the cuprous iodide may be added to the treating acid which is then combined

with the acid corrosion inhibitor, or the cuprous iodide may be added first to the acid corrosion inhibitor which is later combined with the acid. The cuprous iodide may be added to a mixture of treating acid and acid corrosion inhibitor, the order of mixing not being limited to any particular sequence. The cuprous iodide may also be formed in situ in the treating acid or in the treating acid after it has been combined with the acid corrosion inhibitor.

The inhibited treating acid is then pumped through the well tubing or casing into said formation and left in contact with said formation until the desired effect on the formation has been obtained. The inhibited treating acid is then removed from said formation.

Tests have also revealed that cuprous iodide operates to extend the life of the commonly known acid corrosion inhibitors at all temperatures.

The following examples are given to more fully describe certain aspects of the invention set out above and are given primarily for the purpose of illustration; and the invention, in its broader aspects, is not to be construed as limited thereto.

EXAMPLE I

Seven samples (A through H) of 15 percent hydrochloric acid and five samples (I through M) of 30 percent hydrochloric acid are prepared as follows:

Samples A and B (15% HCl) 2.0% by volume HAI-50 (Halliburton brand acid corrosion inhibitor)

Samples C and D (15% HCl) 2.0% by volume Dowell-A110 (Dow Chemical Company acid corrosion inhibitor)

Samples E and F (15% HCl) 2.0% by volume Well-laid-211 (AMOCO brand acid corrosion inhibitor)

Samples G through M contain 2.0% by volume Blend-57 (Halliburton brand acid corrosion inhibitor)

Samples G and H are 15% HCl and Samples I through M are 30% HCl.

Two thousand ppm cuprous iodide by weight of treating acid-acid corrosion inhibitor mixture is added to Samples A, C, E, and G and 5,000; 7,000; 9,000; and 11,000 ppm cuprous iodide by weight of said mixture are added to Samples I, J, K, and L respectively. A coupon of API Type N-80 steel is placed in sufficient acid to produce an acid volume-to-surface area ratio of 90 cc/in.². The samples are heated to 300°F and left for 2 hours at which time the corrosion in lbs./ft.² is measured and recorded.

Table I, below, shows the intensifying effect of various concentrations of cuprous iodide in ppm on three types of acid corrosion inhibitors in 15 percent hydrochloric acid and on one type of acid corrosion inhibitor in 30 percent hydrochloric acid at temperatures of 300°F, clearly illustrating the invention.

TABLE I

Inhibitor Concentration: 2.0%

Test Temperature	300°F
Test Time	2 hours
Metal Type	N-80
Acid	HCl

Acid Volume — Surface Area Ratio: 90 cc/in.²

Sample	Inhibitor	Concentration HCl	Concentration Cu ₂ I ₂ (ppm)	Corrosion lb./ft. ²
A	HAI-50	15%	2,000	0.007

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B	HAI-50	15%	0	0.062
C	Dowell-A110	15%	2,000	0.014
D	Dowell-A110	15%	0	0.054
E	Wellaid-211	15%	2,000	0.019
F	Wellaid-211	15%	0	0.077
G	Blend-57	15%	2,000	0.009
H	Blend-57	15%	0	0.027
I	Blend-57	30%	5,000	0.095
J	Blend-57	30%	7,000	0.062
K	Blend-57	30%	9,000	0.053
L	Blend-57	30%	11,000	0.040
M	Blend-57	30%	0	0.77

EXAMPLE II

Five samples, A through E, of 15% HCl with 0.25 percent by volume acid corrosion inhibitor are prepared. An API Type J-55 metal coupon is placed in each sample. Each sample contains sufficient treating acid-acid corrosion inhibitor mixture to achieve an acid volume-metal surface area ratio of 25 cc/in.². Various amounts of cuprous iodide are placed in the five samples, and the samples are heated to 200°F. The coupons are removed after 17 hours, and the corrosion loss is measured in lbs./ft.². The results in Table II, below, indicate the combination of cuprous iodide with said mixture forms an effective acid corrosion inhibitor intensifier at low concentrations over long periods of time.

TABLE II

Test Temperature — 200°F.

Test Time	17 hours
Metal Type	J-55 (API)
Acid	15% HCl

Acid Volume — Surface Area Ratio: 25 cc/in.²

Sample	Inhibitor	Concentration Cu ₂ I ₂ (ppm)	Corrosion lbs./ft. ²
A	HAI-50	None	0.090
B	0.25%	25	0.029
C	0.25%	50	0.011
D	0.25%	100	0.008
E	0.25%	150	0.006

EXAMPLE III

Four samples (A, B, C, and D) of 15% hydrochloric acid containing 2.0% Blend-57 acid corrosion inhibitor are prepared and heated to 400°F.

Sample A contains 12,500 ppm cuprous iodide.

Sample B contains 15,000 ppm cuprous iodide.

Sample C contains sufficient cuprous oxide and potassium iodide to produce 15,000 ppm cuprous iodide.

Sample D, being the control, contains no acid inhibitor intensifier.

An API Type N-80 metal coupon is placed in each sample prior to heating with sufficient acid present to insure an acid volume-surface area ratio of about 90 cc/in.². The coupons are removed after 2 hours and the corrosion is measured in lbs./ft.².

Table III, below, shows the addition of cuprous iodide to the acid corrosion inhibitor-treating acid mixture reduces acid corrosion to a generally acceptable rate even at high temperatures.

TABLE III

Inhibitor	Blend-57
Test Temperature	400°F
Metal Type	N-80 (API)
Acid	15% HCl
Test Time	2 hours

Acid Volume-Surface Area Ratio: 90cc/in.²

Sample	Concentration Cu ₂ I ₂ (ppm)	Corrosion lbs./ft. ²
A	12,500	0.064

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B	15,000	0.062
C	15,000 (formed in situ)	0.077
D	None	Coupon dissolved

EXAMPLE IV

Eight samples (A through H) of 15 percent hydrochloric acid with 2.0 percent by volume concentration of Blend-57 acid corrosion inhibitor are prepared and heated to 350°F.

Sample A is treated with 10,000 ppm cuprous iodide. Sample B is treated with exact quantities of cuprous oxide and potassium iodide to produce 10,000 ppm cuprous iodide in situ.

Sample C is treated with sufficient cuprous oxide and potassium iodide to produce 10,000 ppm cuprous iodide in situ, plus a 5 percent excess of potassium iodide.

Sample D is treated with sufficient cuprous oxide and potassium iodide to produce 10,000 ppm cuprous iodide in situ, plus a 10 percent excess of potassium iodide.

Sample E is treated with sufficient cuprous oxide and potassium iodide to produce 10,000 ppm cuprous iodide in situ, plus a 15 percent excess of potassium iodide.

Sample F is treated with 12,000 ppm potassium iodide.

Sample G is treated with 6,500 ppm cuprous chloride.

Sample H is treated with 9,375 ppm cuprous oxide. A coupon of API Type N-80 metal is placed in each sample prior to heating. The coupons are removed after 2 hours, and the amount of corrosion in lbs./ft.² is determined.

It is seen from the data recorded in Table IV, below, that a slight excess of from about 5 percent to about 15 percent by weight of I⁻ ions will improve the effect of the cuprous iodide on the acid corrosion inhibitor treating acid mixture. The improvement of cuprous iodide added as a compound and formed in situ over other additives (KI, CuCl and Cu₂O) is also shown.

TABLE IV

Inhibitor	2.0% Blend-57
Test Temperature	350°F
Metal Type	N-80 (API)
Acid	15% HCl
Test Time	2 hours

Acid Volume-Surface Area Ratio: 90 cc/in.²

Sample	Additive	Corrosion lbs./ft. ²
A	10,000 ppm cuprous iodide	0.019
B	10,000 ppm cuprous iodide (in situ) no excess I ⁻ ion	0.024
C	10,000 ppm cuprous iodide (in situ) + 5% excess potassium iodide	0.016
D	10,000 ppm cuprous iodide (in situ) + 10% excess potassium iodide	0.015
E	10,000 ppm cuprous iodide (in situ) + 15% excess potassium iodide	0.016
F	12,000 ppm potassium iodide	0.119
G*	6,500 ppm cuprous chloride	0.215
H*	9,375 ppm cuprous oxide	0.147

*Concentrations sufficient to produce same Cu⁺ ion concentration as 12,500 ppm cuprous iodide (4,175 ppm Cu⁺ ion).

EXAMPLE V

Fourteen samples (1 to 14) of 15 percent hydrochloric acid are prepared. Various concentrations of Blend-57 and HAI-50 acid corrosion inhibitors are added to the samples along with various concentrations of cuprous iodide. A coupon of API Type N-80 metal is

placed in each sample, and the samples are heated to 300°F. The amount of corrosion in lbs./ft.² is measured to determine the effect of various concentrations of cuprous iodide with various concentrations of inhibitor. It is observed, as shown in Table V, below, that a cuprous iodide concentration of about 2,000 ppm is effective to produce satisfactory results in the presence of only about 0.3 percent by volume of Blend-57 and that only about 250 ppm cuprous iodide will produce satisfactory results with a 2.0 percent by volume concentration of HAI-50 at temperatures of about 300°F.

TABLE V

Test Temperature	300°F		
Metal Type	N-80 (API)		
Acid	15% HCl		
Test Time	2 hours		
Acid Volume-Surface Area Ratio: 90 cc/in. ²			
Sample	Inhibitor	Concentration Cu ₂ I ₂ (ppm)	Corrosion lbs./ft. ²
1	None	2,000	>1.5
2	0.1% Blend-57	2,000	1.24
3	0.3% Blend-57	2,000	0.019
4	0.5% Blend-57	2,000	0.017
5	1.0% Blend-57	2,000	0.019
6	1.5% Blend-57	2,000	0.020
7	2.0% Blend-57	2,000	0.009
8	2.0% Blend- 57	0	0.027
9	2.0% HAI-50	0	0.062
10	2.0% HAI-50	250	0.048
11	2.0% HAI-50	500	0.029
12	2.0% HAI-50	1,000	0.010
13	2.0% HAI-50	1,500	0.010
14	2.0% HAI-50	2,000	0.007

EXAMPLE VI

Seven samples (1 through 7) of 15 percent hydrochloric acid are prepared. Varying amounts of cuprous iodide are added to six of the samples, and an API Type J-55 steel coupon is placed in each acid solution and the solutions are heated to 150°F. After 2 hours the coupon is then removed from the acid and weighed to determine the corrosion loss in pounds per square foot. The results in Table VI, below, indicate cuprous iodide may operate as an acid corrosion inhibitor at low temperatures when the corrosion conditions are not severe.

TABLE VI

Test Temperature	150°F	
Metal Type	J-55 steel (API)	
Acid	15% HCl	
Test Time	2 hours	
Metal-Acid Ratio	25 cc/in. ²	
Sample	Concentration	Corrosion
	Cu ₂ I ₂ (ppm)	lbs./ft. ²
1	0	0.037
2	250	0.012
3	500	0.009
4	1,000	0.008
5	1,500	0.008
6	2,500	0.007
7	3,000	0.007

EXAMPLE VII

Eight test samples are prepared using various treating acids and mixtures thereof as corrodents and various nitrogen compounds and acetylenic compounds as acid corrosion inhibitors. Five hundred ppm cuprous iodide is added to each sample. An API Type N-80 metal coupon is placed in each sample solution and each sample is heated to 200°F. After 6 hours the coupon is removed and weighed to determine the acid corrosion loss in lbs./ft.². Table VII, below, indicates cuprous iodide will form an effective inhibited treating acid when combined with an acid corrosion inhibitor and hydrochloric, sulfuric, and acetic acids and mixtures of hydrochloric acid with acetic acid and hydrofluoric acid.

Said table also indicates that an effective inhibited treating acid is formed by the addition of cuprous iodide to a treating acid and various acetylenic compounds and nitrogen compounds.

TABLE VII

Test Temperature Test Time Metal Type			200°F 6 hours N-80 (API)	Corrosion-lbs./ft. ² 500 ppm	
Sample	Inhibitor	Acid	No Cu ₂ I ₂	Cu ₂ I ₂	
1	0.2% Armohib-31 (nitrogen base acid corrosion inhibitor)	10% H ₂ SO ₄	0.070	0.021	
15	2 0.1% MSA Inhibitor (nitrogen base acid corrosion inhibitor)	10% CH ₃ COOH	0.0016	0.0014	
	3 0.2% HAI-50	15% HCl-10% acetic	0.010	0.005	
20	4 0.2% HAI-50	12% HCl-3% HF	0.019	0.004	
	5 0.3% propargyl alcohol (100% active)	15% HCl	0.016	0.010	
	6 0.3% ethyl octynol	15% HCl	0.379	0.044	
	7 0.3% alkyl pyridines	15% HCl	0.031	0.006	
25	8 0.3% rosin amine	15% HCl	0.036	0.006	

EXAMPLE VIII

Twenty-two test samples of 15 percent hydrochloric acid are prepared. The samples are treated with 2.0% Blend-57 acid corrosion inhibitor. Twenty-one of the 22 samples are treated with 7,000 ppm of various compounds of iodine and copper. An API Type N-80 steel coupon is then placed in each sample and each sample is heated to 350°F. After 2 hours the coupons are removed and tested for corrosion loss. Table VIII, below, indicates cuprous iodide forms an effective inhibited treating acid when added to a treating acid and an acetylenic and nitrogen acid corrosion inhibitors, and that cuprous iodide provides an improvement which is clearly better than that provided by other compounds of iodine or copper.

TABLE VIII

	Test Temperature	350°F	
	Test Time	2 hours	
	Type Metal	N-80 (API)	
	Acid	15% HCl	
	Metal-Acid Ratio	90 cc/in. ²	
50	Inhibitor	Iodine or Copper Containing Compound	Corrosion lbs./ft. ²
	2.0% Blend-57	None	>1.5
	2.0% Blend-57	7,000 ppm Cu ₂ I ₂	0.013
	2.0% Blend-57	7,000 ppm FeI ₂	0.182
	2.0% Blend-57	7,000 ppm CsI	0.202
	2.0% Blend-57	7,000 ppm Cu ₂ Br ₂	0.132
55	2.0% Blend-57	7,000 ppm MnI ₂	0.184
	2.0% Blend-57	7,000 ppm Bi(IO ₃) ₃	0.097
	2.0% Blend-57	7,000 ppm ZrOI ₃	0.196
	2.0% Blend-57	7,000 ppm PbI	0.196
	2.0% Blend-57	7,000 ppm BaI ₂	0.077
	2.0% Blend-57	7,000 ppm iodoform	0.082
	2.0% Blend-57	7,000 ppm iodopropane	0.236
60	2.0% Blend-57	7,000 ppm iodomethane	0.320
	2.0% Blend-57	7,000 ppm iodophenol	0.160
	2.0% Blend-57	7,000 ppm BiI ₃	0.175
	2.0% Blend-57	7,000 ppm 1-iodonaphthalene	0.240
	2.0% Blend-57	7,000 ppm 2-iodopropane	0.200
	2.0% Blend-57	7,000 ppm lithium iodide	0.218
65	2.0% Blend-57	7,000 ppm cupric sulfide	0.226
	2.0% Blend-57	7,000 ppm cuprous sulfide	0.241
	2.0% Blend-57	7,000 ppm stannous iodide	0.136
	2.0% Blend-57	7,000 ppm 1-iodo- 2-methylpropane	0.279

EXAMPLE IX

Five samples (A-E) are prepared using 15 percent hydrochloric acid and 2 percent by volume Blend-57 acid corrosion inhibitor.

Sample A contains no cuprous iodide.

Sample B contains 3,000 ppm cuprous iodide.

Sample C contains 5,000 ppm cuprous iodide.

Sample D contains 7,000 ppm cuprous iodide.

Sample E contains 9,000 ppm cuprous iodide.

A coupon of API Type N-80 steel is placed in each sample such that the surface area to acid volume ratio in each sample is about 90 cc/in.². The samples are heated to 300°F where the temperature is maintained for 12 hours. The corrosion loss to the coupon in samples A and B is measured after 2 hours, 6 hours, and 12 hours. The corrosion loss to the coupons in samples C, D and E is measured after 12 hours. The corrosion loss figures in Table IX, below, indicate the improvement in corrosion inhibition of the inhibited treating acid over an acid-acid corrosion inhibitor mixture. Said figures further indicate that the inhibited treating acid provides additional contact time between the corrosive and the metal surface than was available with the acid-acid corrosion inhibitor mixture and that the useful contact time may be increased by increasing the cuprous iodide concentration in the inhibited treating acid.

TABLE IX

Sample	Amount Cu ₂ I ₂ in ppm	Corrosion loss — lbs./ft. ²		
		2 hours	6 hours	12 hours
A	0	0.027	>1.5	Coupon dis- solved
B	3,000	0.008	0.032	0.047
C	5,000	—	—	0.030
D	7,000	—	—	0.028
E	9,000	—	—	0.026

It is clear, then, that the inhibited treating acid herein described may be useful wherever ferrous metal is sought to be protected from the corrosive effects of treating acids at high temperatures. Such uses may include acidizing of subterranean formations such as oil, gas, and water wells, cleaning industrial machinery, pickling steel in acid and others. It will be apparent that many widely different uses may be made of the method of the present invention without departing from the spirit and scope thereof and, therefore, it is not intended to be limited except as indicated in the appended claims.

We claim:

1. An inhibited treating acid consisting essentially of a treating acid selected from the group consisting of hydrochloric acid, sulfuric acid, mixtures of hydrochloric acid and acetic acid, hydrofluoric acid and hydrochloric acid, sulfuric acid and acetic acid, sulfuric acid and hydrofluoric acid, and mixtures thereof,

cuprous iodide present in a concentration of from about 25 ppm by weight of said treating acid to about 25,000 ppm by weight of said treating acid, and

an acid corrosion inhibitor selected from the group consisting of acetylenic alcohols and mixtures thereof and mixtures of organic nitrogen compounds and acetylenic alcohols.

2. The inhibited treating acid of claim 1 wherein said acid corrosion inhibitor is present in a concentration of from about 0.1 percent to about 2.5 percent by volume of said treating acid.

3. The inhibited treating acid of claim 1 wherein said treating acid is present in strengths of from about pH 6.5 to about 35 percent by weight of treating acid in water.

4. The inhibited treating acid of claim 1 wherein said acid corrosion inhibitor is selected from said acetylenic alcohols and mixtures thereof.

5. The method of protecting a ferrous metal surface against acid corrosion which comprises the step of:

contacting said surface with an inhibited treating acid consisting essentially of:

a treating acid selected from the group consisting of hydrochloric acid, sulfuric acid, mixtures of hydrochloric acid and acetic acid, hydrofluoric acid and hydrochloric acid, sulfuric acid and acetic acid, sulfuric acid and hydrofluoric acid, and mixtures thereof;

an acid corrosion inhibitor selected from the group consisting of acetylenic alcohols and mixtures thereof, and mixtures of organic nitrogen compounds and acetylenic alcohols; and

cuprous iodide present in a concentration in the range of about 25 ppm by weight of treating acid to about 25,000 ppm by weight of treating acid wherein said contacting of said surface is conducted at temperatures of up to about 450°F.

6. The method of claim 5 wherein said treating acid is present in strengths of from about pH 6.5 to about 35% by weight of treating acid in water.

7. The method of claim 5 wherein said acid corrosion inhibitor is present in a concentration of from about 0.1 percent to about 2.5 percent by volume of treating acid.

8. The method of protecting a ferrous metal surface against acid corrosion which comprises the steps of:

contacting said surface with an inhibited treating acid consisting essentially of

a treating acid selected from the group consisting of hydrochloric acid, sulfuric acid, mixtures of hydrochloric acid and acetic acid, hydrofluoric acid and hydrochloric acid, sulfuric acid and acetic acid, sulfuric acid and hydrofluoric acid, and mixtures thereof

a solution prepared by combining an acid soluble salt of iodine and an acid soluble salt of copper, and

an acid corrosion inhibitor selected from the group consisting of acetylenic alcohols and mixtures thereof and mixtures of organic nitrogen compounds and acetylenic alcohols;

and allowing said salts to form cuprous iodide in a concentration in the range of about 25 ppm by weight of treating acid to about 25,000 ppm by weight of treating acid.

wherein said contacting of said surface is conducted at temperatures of up to about 450°F.

9. The method of inhibiting acid corrosion of ferrous metal surfaces at temperatures below about 150°F, which comprises the steps of:

contacting a ferrous metal surface with an inhibited treating acid consisting essentially of:

a solution prepared by adding an acid soluble salt of iodine and an acid soluble salt of copper to an

acid selected from the group consisting of hydrochloric acid, sulfuric acid, mixtures of hydrochloric acid and acetic acid, hydrofluoric acid and hydrochloric acid, sulfuric acid and acetic acid, sulfuric acid and hydrofluoric acid, and mixtures thereof; and

allowing said salts to form cuprous iodide, wherein said cuprous iodide is allowed to form in concentrations of from about 50 ppm to about 3,000 ppm by weight of acid, and further, wherein there is utilized an excess of from about 5 percent to about 15 percent by weight of said acid soluble salt of iodine.

10. The method of claim 9 wherein said acid soluble salt of iodine is potassium iodide.

11. The method of claim 9 wherein said acid soluble salt of copper is selected from the group consisting of cupric sulfate, cuprous oxide, cuprous chloride and cupric chloride.

12. The method of claim 9 wherein said acid is present in a strength of from about pH 6.5 to about 35 percent by weight of acid in water.

13. The method of protecting a ferrous metal surface against acid corrosion which comprises the steps of: contacting said surface with an inhibited treating acid consisting essentially of

a treating acid selected from the group consisting of hydrochloric acid, sulfuric acid, mixtures of hydrochloric acid and acetic acid, hydrofluoric acid and hydrochloric acid, sulfuric acid and acetic acid, sulfuric acid and hydrofluoric acid, and mixtures thereof,

a solution prepared by combining an acid soluble salt of iodine, and an acid soluble salt of copper, wherein there is utilized an excess of from about

5 percent to about 15 percent by weight of said acid soluble salt of iodine, and

an acid corrosion inhibitor selected from the group consisting of acetylenic alcohols and mixtures thereof; mixtures of organic nitrogen compounds and acetylenic alcohols; and organic nitrogen compounds selected from mono, di, and tri-alkyl amines having from two to six carbon atoms in each alkyl moiety, six membered N-heterocyclic amines, alkyl pyridines having from one to five nuclear alkyl substituents per pyridine moiety wherein said alkyl substituents have from one to 12 carbon atoms, rosin amines, and mixtures thereof,

and allowing said salts to form cuprous iodide in a concentration in the range of about 25 ppm by weight of treating acid to about 25,000 ppm by weight of treating acid,

wherein said contacting of said surface is conducted at temperatures of up to about 450°F.

14. The method of claim 13 wherein said acid soluble salt of iodine is potassium iodide.

15. The method of claim 13 wherein said acid soluble salt of copper is selected from the group consisting of cupric sulfate, cuprous oxide, cuprous chloride and cupric chloride.

16. The method of claim 13 wherein said treating acid is present in a strength of from about pH 6.5 to about 35 percent by weight of acid in water.

17. The method of claim 13 wherein said acid corrosion inhibitor is present in a concentration of from about 0.1 percent to about 2.5 percent by volume of treating acid.

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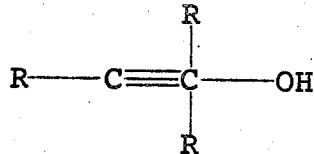
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Patent No. 3,773,465 Dated November 20, 1973

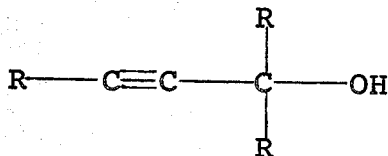
Inventor(s) Bill R. Keeney and Joe W. Johnson, Jr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In Column 3, lines 22 through 24: Delete the formula



and insert therefor the formula



Signed and sealed this 23rd day of April 1974.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

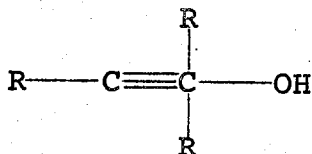
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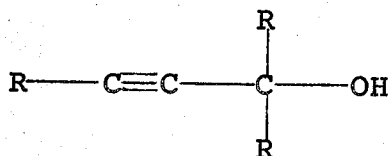
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