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INHIBITOR COMPOSITION AND METHOD OF INHIBITING ACID ATTACK ON METAL IN THE ACIDIZING OF WELLS

George S. Gardner, Elkins Park, Frank E. Manson, Lansdale, and Edgar S. Hayman, Jr., Doylestown, Pa., assignors to Amchem Products, Inc., Ambler, Pa., a corporation of Delaware

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2 Claims. (Cl. 252—149)

This invention relates to inhibitor compositions for preventing or greatly minimizing acid attack on metal surfaces. More particularly, it relates to the prevention of corrosive attack of non-oxidizing acids under conditions of high temperature and high acid concentration such as are often encountered in the acidizing of oil wells.

As is well known in this art, acidizing operations are carried out on both new and used well formations in order to facilitate recovery of the petroleum. The acidizing technique involves the introduction into the well formation of relatively strong acid solutions and this frequently leads to severe attack by the acid components of these solutions on the well casing and tubing.

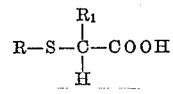
Various types of corrosion inhibitors have been incorporated into the acidizing solutions in an effort to retard or eliminate their attack on the metal surfaces within the well. Typical examples of such inhibitors are disclosed in United States Patents 1,719,649; 2,510,063; 2,564,759 and 2,758,970, the latter three patents all referring to derivatives of rosin amine. However, experience with these inhibitors in well acidizing operations has indicated that, although some degree of protection is afforded, the over-all protection is insufficient, especially with regard to what is known as "pitting" attack on the well tubing. Furthermore, a greater trend toward inefficiency is encountered with these inhibitors with increased temperatures in the well formations and in this connection attention is called to the fact that the temperature in well formations is related proportionally to the depth thereof. For instance, the temperatures encountered at the bottom of a 10,000 ft. well are often found to be in the neighborhood of about 225 to 235° F. whereas in wells of about 15,000 ft. the temperatures encountered are often in the neighborhood of 300 to 350° F. Beyond this, present well technology is toward the exploitation of ever deeper well formations and this emphasizes the need for highly effective inhibitors which are stable not only in high concentrations of acid but also at elevated temperatures.

In attempting to circumvent the difficulty arising with increase in temperature the art has made use of arsenic base inhibitors. Initially these inhibitors were apparently successful in well acidizing operations, especially where the formation contained no hydrogen sulfide. However, it was soon discovered that the arsenic contaminant, present in the crude petroleum recovered from such operations, poisoned the catalysts employed in subsequent petroleum refinement, and this drawback, together with the toxic nature of arsenical solutions, has led to a virtual abandonment of these inhibitor systems.

With the foregoing in mind the principal objects of the present invention reside in the provision of improved inhibitor compositions for reducing acid attack on metal surfaces as well as in the provision of an improved method of preventing corrosion of metal surfaces which are exposed to the effects of high concentrations of acid at relatively high temperatures such as are encountered in the deeper oil wells.

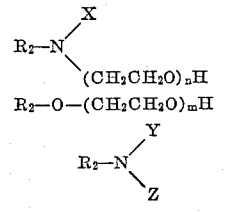
Another object of the invention is the provision of a method for inhibiting acid attack on the so-called "high-strength" alloys used in well tubing.

The present invention is based upon the discovery that the corrosive action of non-oxidizing acids on metal surfaces can be substantially reduced, even at elevated temperatures and at high acid concentrations and even in the presence of hydrogen sulfide, by employing an inhibiting composition which consists essentially of a mixture of certain mercapto acid compounds in combination with certain organic corrosion inhibitors familiar to the art. The mercapto acid compounds which are useful in our improved inhibiting admixture are represented by the formula:



where R is a radical selected from the group consisting of phenyl, benzyl, naphthyl and naphthyl methyl and the halo- and alkyl-substitution products thereof; and R_1 is selected from the group consisting of hydrogen and lower alkyl.

The organic corrosion inhibitor component which is useful in our improved inhibiting admixture should be selected from the group consisting of (*a*) products prepared by the condensation of aldehydes such as aldol, acetaldehyde, butyraldehyde, heptaldehyde, furfuraldehyde and benzaldehyde with amines such as alpha-naphthylamine, diphenylguanidine, aniline, o-toluidine, and diethylamine (organic corrosion inhibitors of this type are described in U.S. Pat. 1,719,649 above referred to), and (*b*) compound represented by the following formulas:

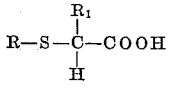


where R_2 is a radical selected from the group consisting of abietyl, hydroabietyl and dehydroabietyl; X is hydrogen or the radical $(CH_2CH_2O)_nH$; Y is CH_2A; Z is from the group consisting of hydrogen and the radical CH_2A; A represents alpha-ketonyl groups, *m* is an integer of from 9 to 38; and *n* is an integer of from 2 to 10. The preparation and/or use of compounds of this latter group are described in United States Patents 2,510,063; 2,564,759 and 2,758,970 above referred to, the disclosures of which patents are incorporated herein by way of reference.

Hereinafter the broad term "corrosion inhibitor compound" should be interpreted as identifying any product resulting from the processes of the four patents referred to above unless some other meaning is made clear by the context.

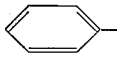
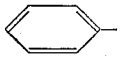
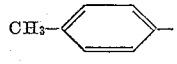
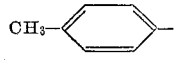
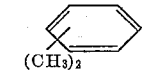
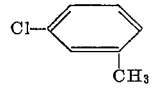
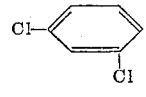
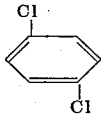
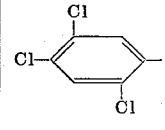
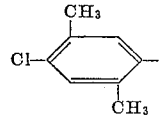
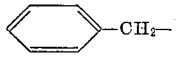
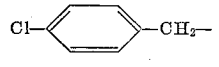
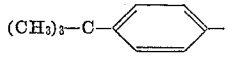
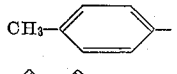
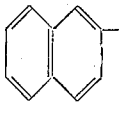
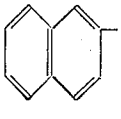
The amount of the mercapto acid compound which must be used in conjunction with the corrosion inhibitor compound has been found to lie within the range of 0.03 to 1.0% of the total acid solution. Use of less than about 0.03% by weight of the mercapto acid compound, based on the total volume of acid solution, fails to guard effectively against a pitting type attack. Conversely, use of more than about 1% (weight/volume) of the mercapto compound does not appear to offer any additional advantages and actually increases the cost of such inhibitor compositions. A preferred range of mercapto acid compound has been found to be 0.08 to 0.2% by weight based on the volume of the acid solution, since it has been found that all of the mercapto acid compounds falling under this disclosure provide optimum corrosion protection when employed within this range and in conjunction with an organic corrosion inhibitor such as described above.

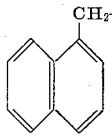
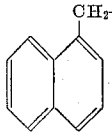
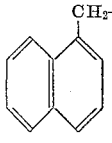
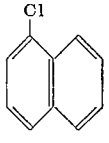
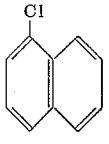
Typical examples of mercapto acid compounds which have been found suitable for use in the present invention are presented below in Table I, but these compounds are not to be construed as a limitation of the disclosure except as defined by the generic formula:



where R and R_1 are as defined above.

TABLE I

Compound No.	R	R_1
I		H
II		CH_3
III		H
IV		H
V		i-C_3H_7
VI [1]		H
VII		H
VIII		H
IX		C_2H_5
X		H
XI		H
XII		H
XIII		H
XIV		H
XV		n-C_4H_9
XVI		H
XVII		C_2H_5

Compound No.	R	R_1
XVIII		H
XIX		CH_3
XX		C_2H_5
XXI		H
XXII		CH_3

[1] Mixed isomers of xylyl mercapto acetic acids.

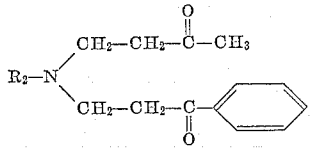
Insofar as the organic corrosion inhibitor component or components of our improved inhibiting admixtures are concerned we would like to point out that use of these components as disclosed in the patents noted above has become so widely accepted for general inhibiting purposes that any one skilled in this art can easily determine the optimum amount of the compound required for any particular set of operating conditions. Since this will vary within the well accepted knowledge of the art no specific quantity of these compounds is specified for the present invention. The point which is of importance insofar as our invention is concerned arises in connection with the quantity of mercapto acid compound which should be included in the admixture and even as to this component of our admixture only a lower limit of content is of any real importance except insofar as cost may be a factor. Large quantities of the mercapto acid compound do not seem to do any harm but beyond a certain quantity they do not seem to yield any marked advantage. By way of a minimum quantity we have found that it should be at least 0.03% by weight based on the total volume of the acid solution employed in the acidizing operation. We have further found that beyond about 1% by weight no marked additional improvement has been noted and, as indicated above, the preferred range from the standpoint of efficiency with relation to economy is from about 0.08 to 0.2% by weight based on the total volume of acid solution used in the acidizing operation.

In order to demonstrate more fully the improved performance obtained with the compositions of the present invention there are presented below a series of results showing the inhibiting properties of various mercapto acid compounds as used alone, various organic corrosion inhibitor compounds as described above and used alone, as well as mixtures of both of these types of compounds, which results are included by way of example and are not intended to be construed as a limitation of this invention. In all of the reported tests it will be noted that N–80 type tubing was utilized since this particular

grade, although not the subject of an API composition specification is widely used in the petroleum industry, and is on of the most difficult alloys to protect from corrosive environments since it is particularly susceptible to a pitting type attack.

An acid solution was prepared containing 15% by weight of hydrochloric acid and was used as the corroding medium on sections of N–80 tubing which were exposed thereto for 4-hour periods at temperatures of 250° F. The corrosive effect of this uninhibited solution is recorded below in Table II. Mercapto acid compound was then added to portions of this 15% hydrochloric solution to yield acid solutions containing the amount of mercapto compound indicated in the table. The mercapto compounds referred to in the following tables are all identified by numbers which refer to similar numbers in Table I for identification of these compounds.

A corrosion inhibitor compound, prepared in accordance with Example I of U.S. Patent 2,758,970, except that the reaction was carried out with acetone and acetophenone added consecutively in order to obtain the reaction product corresponding to the structure:



where R_2 is as described above, was then admixed with the 15% by weight of hydrochloric acid solution as prepared above to yield an acid solution containing 0.5% by weight of the corrosion inhibitor compound. This acid solution was then used as the corroding medium on sections of N–80 tubing which were exposed thereto for the time and temperature noted above. The results of this test are reported below in Table II.

Various mercapto acid compounds were then added at a level of 0.2% (weight/volume) to the hydrochloric acid solution containing 0.5% (weight/volume) of the organic corrosion inhibitor compound noted above. The resulting corrosion data are recorded below in Table II, where, in addition to the weight loss figures which are calculated on the basis of a 24-hour test, there is also presented a description of the type of corrosive attack observed for each of the test results.

TABLE II

[Using 15% (weight/weight) of hydrochloric acid]

Inhibitor employed			Corrosion results	
Percent organic corrosion inhibitor	Mercapto acid		Weight loss, lbs./ft.²/ 24 hours	Pitting
	Compound	Percent		
None	None	-------	11.10	Severe.
None	IV	1.0	10.30	Do.
None	XI	1.0	11.40	Do.
None	XIV	1.0	10.50	Do.
0.5	None	-------	0.545	Do.
0.5	I	0.2	0.090	None.
0.5	III	0.2	0.125	Do.
0.5	IV	0.2	0.096	Do.
0.5	VI	0.2	0.132	Do.
0.5	VII	0.2	0.159	Do.
0.5	VIII	0.2	0.136	Do.
0.5	XI	0.2	0.114	Do.
0.5	XII	0.2	0.141	Do.
0.5	XIV	0.2	0.062	Do.
0.5	XV	0.2	0.056	Do.
0.5	XVI	0.2	0.102	Do.
0.5	XVII	0.2	0.060	Do.
0.5	XVIII	0.2	0.161	Do.
0.5	XIX	0.2	0.095	Do.
0.5	XX	0.2	0.129	Do.
0.5	XXI	0.2	0.101	Do.

A solution was prepared containing 15% by weight of hydrochloric acid and was used as the corroding medium on sections of N–80 tubing which were exposed thereto for 6 hours at temperatures of 200° F. The corrosive effect of this uninhibited acid solution is reported below in Table III.

Three mercapto acid compounds, identified by numerals which correspond to similar numerals in Table I, were added at levels of 0.2 and 1% (weight/volume) to a 15% (weight/weight) hydrochloric acid solution. The effect of these compounds on retarding corrosion of N–80 tubing under the conditions of time and temperature reported immediately above is shown in Table III.

A corrosion inhibitor was prepared by the reaction of 32 parts of orthotoluidine with 32 parts of 37% formaldehyde solution and 38 parts of 20° Baumé hydrochloric, and then adding 98 parts of 37% formaldehyde solution to the mixture in accordance with the disclosure of U.S. Pat. 1,719,649. This corrosion inhibitor compound was then formulated with 15% by weight of hydrochloric acid to a concentration of 1.0% by weight of the corrosion inhibitor. This inhibited acid solution was then used as the corrosive medium in tests to determine the effects thereof on N–80 type tubing exposed thereto at temperatures of 200° F. for 6 hours. The results of this test are reported below in Table III.

Various mercapto compounds from the list in Table I were then added at various percentage levels (weight/volume) to the hydrochloric acid solution containing organic corrosion inhibitor compound as discussed in the preceding paragraph and the conditions and results of these tests are reported in Table III below:

TABLE III

[Using 15% (weight/weight) of hydrochloric acid]

Inhibitor employed			Corrosion results	
Percent organic corrosion inhibitor	Mercapto acid		Weight loss, lbs./ft.²/ 24 hours	Pitting
	Compound	Percent		
None	None	-------	3.43	Severe.
None	IV	0.2	3.40	Do.
None	IV	1.0	2.86	Do.
0.8	IV	0.03	0.045	None.
0.6	IV	0.03	0.112	Do.
1.0	IV	0.1	0.097	Do.
0.8	IV	1.0	0.034	Do.
0.6	IV	1.0	0.046	Do.
0.6	None	-------	0.615	Severe.
0.8	do	-------	0.172	Do.
1.0	do	-------	0.201	Moderate.
None	XI	0.2	3.48	Severe.
None	XI	1.0	3.18	Do.
None	XIV	0.2	3.25	Do.
None	XIV	1.0	3.80	Do.
1.0	XIV	0.1	0.093	None.

Using the same solutions as employed in Table III, a further series of corrosion tests were run wherein the hydrochloric acid solutions were in all cases saturated with hydrogen sulfide gas. The same operating conditions, namely, 6 hours at a temperature of 200° F. were employed. These results are summarized in Table IV.

TABLE IV

[Using 15% (weight/weight) of hydrochloric acid saturated with hydrogen sulfide gas]

Inhibitor employed			Corrosion results	
Percent organic corrosion inhibitor	Mercapto acid		Weight loss, lbs./ft.²/ 24 hours	Pitting
	Compound	Percent		
None	None	-------	5.26	Severe.
None	IV	1.0	2.95	Do.
None	XI	1.0	3.48	Do.
None	XIV	1.0	4.87	Do.
1.0	None	-------	0.208	Moderate.
1.0	IV	0.1	0.109	None.
1.0	XI	0.1	0.113	Do.
1.0	XIV	0.1	0.122	Do.
1.0	XVI	0.1	0.083	Do.

A corrosion inhibitor compound such as used in Example I of U.S. Pat. 2,510,063 and which is sold commercially under the trade name "Polyrad 1110A" [1] by the Hercules Powder Company of Wilmington, Delaware, was formulated with 15% by weight of hydrochloric acid to produce a testing solution containing 1.0% of the corrosion inhibitor compound. This solution was then used as the corrosion medium on N–80 tubing exposed thereto for 4 hours at 250° F. Several of the mercapto acid compounds listed in Table I were then added to portions of this testing solution and the resulting data from these inhibitor compositions as well as from the use of the individual components alone are reported in Table V.

TABLE V

[Using 15% (weight/weight) of hydrochloric acid]

Inhibitor employed			Corrosion results	
Percent organic corrosion inhibitor	Mercapto acid		Weight loss, lbs./ft.²/ 24 hours	Pitting
	Compound	Percent		
None	None		3.43	Severe.
1.0	do		0.966	Do.
None	I	0.2	3.34	Do.
None	IV	0.2	3.40	Do.
None	VIII	0.2	3.18	Do.
None	XI	0.2	3.48	Do.
None	XIV	0.2	3.25	Do.
None	XVI	0.2	3.62	Do.
1.0	I	0.2	0.373	Very slight.
1.0	IV	0.2	0.472	Do.
1.0	VIII	0.2	0.433	Do.
1.0	XI	0.2	0.457	Do.
1.0	XIV	0.2	0.428	Do.
1.0	XVI	0.2	0.518	Do.

It will be noted from the various corrosion tests reported above that the mercapto acid compounds when used alone exhibit essentially no noticeable inhibiting property, but when these are combined with the corrosion inhibitor compounds as decribed above, improved corrosion protection results not only with respect to the reduced weight loss of the metal but also with respect to an elimination or substantial reduction of the pitting type attack on the metal surfaces. It is thus quite apparent that the inhibitor compositions of this invention are capable of eliminating or substantially retarding the corrosive attack of non-oxidizing acids on metal surfaces even at high temperatures.

It is within the purview of this invention to provide new, concentrated inhibitor formulations containing both the organic corrosion inhibitor compounds and the mercapto acid compounds as described above. These concentrated formulations have been found desirable since they may be supplied directly to the site where they are to be used and simply added to the acidic solutions being employed in the acidizing operations.

Since both types of these compounds have been found to possess varying degrees of water-solubility—ranging from a few tenths of 1 percent or even lower, to as much as essentially complete water-solubility—the method of formulating will depend entirely upon the particular choice of compounds used. For example, where both the corrosion inhibitor compound and the mercapto acid compound possess sufficient water-solubility in the amounts used, they may simply be blended to form a concentrated inhibitor admixture. However, where one or more of the compounds have limited solubility, or are substantially corrosion inhibitor compounds and the mercapto acid insoluble in water, it has been found most practical and convenient to formulate these compounds into a non-aqueous solution of a non-ionic surface active agent of the polyalkoxylated-alkylated phenol type. It has been found that alkylated phenols containing from 8 to 10 carbon atoms in the alkyl group and from 7 to as high as 50 mols of ethylene and/or propylene oxide per mol of the alkyl phenol, provide completely satisfactory solubilizing action for these inhibitor compounds.

Where a concentrated admixture of corrosion inhibitor compound and mercapto acid compound is used, these ingredients should be present in a weight/weight ratio of from 0.05 to 0.5 part of the mercapto acid compound for each part of the corrosion inhibitor compound.

Where the polyalkoxylated-alkylated phenol type surface active agent is employed for solubilizing action, it is preferred that from about 4 to 40% (weight/weight) of this agent be utilized in the concentrated inhibitor formulation. The balance of this formulation, that is from 60 to 96% thereof, then consisting of an admixture of the mercapto acid compound and the corrosion inhibitor compound within the ratio noted above.

In order to illustrate such concentrated inhibitor formulations as falling within this disclosure, there are listed below several preferred formulations which are presented by way of example but are in no way intended to be construed as a limitation of this invention. The parts indicated are parts by weight of the total composition.

Example I

	Parts
Polyrad 1110A [1]	90
4-chlorobenzylmercapto-acetic acid (Compound No. XIII in Table I)	10

Example II

	Parts
Corrosion inhibitor compound of Example 1 of U.S. Pat. 2,758,970	620
2-(4-methylphenylmercapto)-2-isopropyl-acetic acid (Compound No. V in Table I)	100
Tergitol NP–35 [2]	100

Example III

	Parts
Corrosion inhibitor compound of Example 7 of U.S. Pat. 2,758,970	650
4-methylphenylmercapto-acetic acid (Compound No. IV in Table I)	75
Tergitol NP–44 [3]	68

Example IV

	Parts
Corrosion inhibitor compound [4]	794
2-naphthylmercapto-acetic acid (Compound No. XVI in Table I)	42
Triton X–305 [5]	42

[1] Reputed to be a rosin amine-ethylene oxide condensation product having 11 total mols of ethylene oxide and 10% free rosin amine D, as sold by the Hercules Powder Company.

[1] Polyrad 1110A is reputed to contain 11 mols of ethylene oxide per mol of rosin amine D, as sold by the Hercules Powder Company. (See description at top of column 7.)

[2] Reputed to be a condensation product of nonylphenol with 15 mols of ethylene oxide as sold by Union Carbide Company.

[3] Reputed to be a condensation product of nonylphenol with 40 mols of ethylene oxide as sold by Union Carbide Company.

[4] Prepared by reacting 32 parts of o-toluidine with 32 parts of 37% formaldehyde solution and 38 parts of 20° Bé. hydrochloric acid, and then adding 98 parts of 37% formaldehyde solution to the mixture as disclosed in U.S. Pat. 1,719,649.

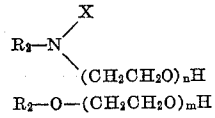
[5] Reputed to be a condensation product of octylphenol with 30 mols of ethylene oxide as sold by Rohm & Haas Company.

We claim:

1. A concentrated inhibitor composition consisting essentially of an admixture of organic corrosion inhibitor from the class consisting of

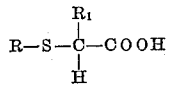
(*a*) organic condensation product resulting from the reaction of aldehyde from the class of aldol, acetaldehyde, butyraldehyde, heptaldehyde, furfuraldehyde and benzaldehyde with amine from the class of alpha-naphthylamine, diphenylguanidine, aniline, o-toluidine and diethylamine, and

(*b*) compound selected from the class consisting of:



and

where R_2 is a radical selected from the group consisting of abietyl, hydroabietyl and dehydroabietyl; X is from the group consisting of hydrogen and the radical $(CH_2CH_2O)_nH$; Y is CH_2A; Z is from the group consisting of hydrogen and the radical CH_2A; in which radicals A represent alpha ketonyl groups, *m* is an interger of from 9 to 38; and *n* is an integer of from 2 to 10, together with mercapto acid compound represented by the formula:



where R is a radical selected from the group consisting of phenyl, benzyl, naphthyl and naphthyl methyl and the halo and alkyl substitution products thereof; and R_1 is selected from the group consisting of hydrogen and lower alkyl; the said mercapto acid compound being present in a weight/weight ratio of from 0.05 to 0.5 part for each part of organic corrosion inhibitor compound.

2. A composition according to claim 1 containing also a non-aqueous solution of polyalkoxylated-alkylated phenol containing from 8 to 10 carbon atoms in the alkyl group and from 7 to 50 mols of oxide from the class of ethylene and propylene oxides per mol of the alkyl phenol, the quantity of said solution being from about 4 to 40% (weight/weight) of the composition with the balance being mercapto acid compound plus organic corrosion inhibitor.

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