United States Patent Office 2,944,969 Patented July 12, 1960

2,944,969

PREVENTION OF RUST AND CORROSION

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No Drawing. Filed Feb. 6, 1957, Ser. No. 638,428

10 Claims. (Cl. 252—8.55)

The present invention is concerned with a method of preventing corrosion of metals when exposed to contact with corrosive fluids and particularly corrosive fluids of the kind found in the product refining and transportation of petroleum hydrocarbons and the like. The process is characterized by the fact that there is added to the fluid a compound described in detail subsequently.

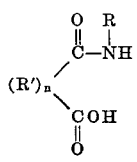
More specifically, the present invention is concerned with a method for inhibiting the corrosion of ferrous metals by hydrocarbon fluids which are inherently corrosive in nature due to the presence of one or more materials of the kind recognized to be corrosive, such as hydrocarbon fluids containing water, hydrogen sulfide, carbon dioxide, organic acids containing 2 to 4 carbon atoms, etc., and combinations of such corrosion causing substances either alone or in combination with other corrosive materials such as, for example, oxygen, etc., and particularly in presence of both water and oxygen.

Generally speaking, one of the principal applications is in the primary production of petroleum by reducing the corrosiveness to corrodible ferrous metal of a corrosive petroliferous well fluid including moisture and hydrogen sulfide which comprises introducing into said fluid a corrosion inhibiting compound of the kind herein described.

However, in secondary recovery processes, i.e., such as flooding processes and particularly where flood water is used over again and again, it is not unusual to have oxygen present although oxygen may occur in a refining or transportation system by mere leakage and thus the invention from this particular standpoint can be restated as a method of inhibiting corrosion of ferrous metals by hydrocarbon fluids.

More specifically, the present invention is concerned with a method for inhibiting corrosion of ferrous metals by hydrocarbon fluids containing water and a member of the group of corrosive materials consisting of hydrogen sulfide, carbon dioxide, organic acids containing 2 to 4 carbon atoms per molecule, combinations of these materials with each other, combinations of each of said corrosive materials with oxygen, and combinations of said materials with each other and oxygen, comprising adding to said fluids at least 5 parts per million of a nonbasic amidic acid as herein described.

Thus, in many instances the invention consists of conventional procedure for adding at least 5 parts per million of a nonbasic amidic acid having the formula



in which R represents a hydrocarbon radical having not over 22 carbon atoms, R' represents a member of the class of hydrocarbon radicals having not over 8 carbon atoms, and n represents a numeral not greater than one and including zero.

The further limitation in regard to R' is that the hydrocarbons be selected from the class of aryl, aliphatic and alicyclic hydrocarbon radicals.

The herein described corrosion inhibitor is particularly effective as a corrosion inhibiting agent in the oil industry. The use of such corrosion inhibitors is common practice. See, for example, U.S. Patents Nos. 2,736,658 dated February 28, 1956, to Pfohl et al.; 2,756,211, dated July 24, 1956, and 2,727,003 dated December 13, 1955, and both to Hughes, and also U.S. Patent 2,614,980 to Lytle, dated October 21, 1952.

As to the employment of corrosion inhibiting agents in the petroleum industry one need only refer to excerpts from the above patents as clearly indicating the field of application. For instance, the following excerpt from U.S. Patent 2,736,658 applies in the instant situation:

"It is a general object of this invention to provide a novel method for protecting metal surfaces from corrosion involving the use of a class of corrosion inhibitors whose unexpectedly superior corrosion inhibiting properties were discovered in the course of the experimental work leading to the present invention. More specifically, it is an object of this invention to provide a method and a means for protecting ferrous metal surfaces against corrosion by the action of oxygen and water. In this connection, it is an object of this invention to provide a corrosion inhibiting method which is capable of protecting ferrous metal surfaces which are normally in contact with atmospheric air, and also ferrous metal surfaces which are normally or at least periodically in contact with liquids containing dissolved water, oxygen and other corrosion compounds or elements. It is a still further object of this invention to provide corrosion inhibitor compositions for use in the method of this invention, and particularly corrosion inhibitor compositions in which the liquid or solid carrier for the corrosion inhibitor cooperates with the inhibitor to increase its effectiveness in protecting metal surfaces, and particularly ferrous metal surfaces."

Again reference is made to an excerpt from aforementioned U.S. Patent No. 2,727,003 which also applies with equal force and effect in regard to the instant invention:

"It should also be pointed out that the corrosiveness of oil well brines will vary from well to well, and the proportion of corrosion inhibiting agent added to the well fluids should also be varied from well to well. Thus, in some wells it may be possible to effectively control corrosion by the addition of as little as 10 p.p.m. of my new compositions to the well fluids, whereas in other wells, it may be necessary to add 200 p.p.m. or more.

"In using my improved compositions for protecting oil well tubing, casing, and other equipment which comes in contact with the corrosive oil-brine production, I find that excellent results may be obtained by injecting an appropriate quantity of a selected composition into a producing well so that it may mingle with the oil-brine mixture and come into contact with the casing, tubing, pumps and other producing equipment. I may, for example, introduce the inhibiting composition into the top of the casing, thus causing it to flow down into the well and thence back through the tubing, etc. In general, I have found that this procedure suffices to inhibit corrosion throughout the entire system of production, and collection, even including field tankage."

As a matter of fact what is said above is in essence the equivalent of what appears in U.S. Patent Re. 23,227, dated May 9, 1950, to Blair et al., at columns 9, 10 and 11.

Specific reference is made to aforementioned U.S. Pat-

ent 2,756,211. Indeed, with a slight change in text the following is essentially a verbatim excerpt of a paragraph in said patent:

"In case serious emulsion or gel problems are encountered, demulsifiers may be added. This is important not only to avoid the troublesome emulsions and gels themselves, but also to improve corrosion inhibition. The explanation of less effective corrosion inhibition in the presence of emulsions apparently is that the inhibitor is somewhat surface-active. That is, it is concentrated at interfacial surfaces. Since this surface is great in an emulsion, most of the inhibitor will be concentrated in these interfaces and little will remain in the body of the oil for deposition on the metal surfaces. In many wells, oil-in-water type emulsions often occur naturally. In such wells the inhibitors herein described tending to form water-in-oil type emulsions, often decrease the emulsion problems naturally present. Thus, in addition to being effective corrosion inhibitors the herein described products tend to eliminate emulsion problems which sometimes appear when some of the present day inhibitors are used in oil wells or refinery processing."

For purpose of convenience, what is said hereinafter will be divided into three parts:

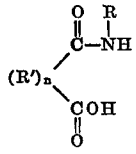
Part 1 is concerned with the manufacture of the herein described nonbasic amidic acids;

Part 2 is concerned with the structure of the herein defined nonbasic amidic acids in comparison with somewhat similar compounds which are differentiated by being surfactant in nature, and

Part 3 is concerned with the use of the herein described amidic acids as corrosion inhibitors.

PART 1

Reference is made to the structural formula of the amidic acids which can be employed in the herein described method. Obviously, in the instance where n is zero the acid is oxalic acid. The following examples illustrate derivatives of this type in which n is one and which conform to the formula:



However, in the majority of cases the value of n is unity as differentiated from zero and the radical R' may contain as many as 6 carbon atoms.

Example 1a

A mixture of 516 grams of Armeen 8 (Armour & Co., octyl amine) and 664 grams of terephthalic acid, in the presence of sufficient xylene to maintain a pot temperature of 200° C. (approximately 15 ml.), was brought to vigorous reflux in a flask equipped with an agitator, thermometer, and water separator. Heating was continued until 72 grams of water has been removed which required approximately fifteen hours.

Example 2a

A mixture of 258 grams of Armeen 8 and 200 grams of succinic anhydride were allowed to react, with vigorous stirring, until the exothermic reaction has subsided. The temperature was then 85° C. The reaction mixture was then heated to 130° C. for ten minutes and then allowed to cool.

Example 3a

The reaction was allowed to proceed as in Example 2a except 370 grams of Armeen 12 were used in place of the Armeen 8.

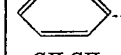
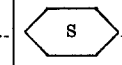
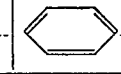
Example 4a

The reaction was allowed to proceed as in Example 2a except 198 grams of cyclohexyl amine was used in place of the Armeen 8 and a final maximum temperature of 110° C. was used.

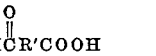
Example 5a

The reaction was allowed to proceed as in Example 4a except 186 grams of aniline was used in place of the cyclohexyl amine.

TABLE I

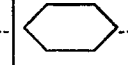
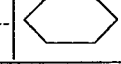
Ex. No.	n	R'	R	Identification used in Tests in Part 3 succeeding
1a	1		C_8H_{17}—	A 33038
2a	1	—CH_2CH_2—	C_8H_{17}—	A 33032
3a	1	—CH_2CH_2—	$C_{12}H_{25}$—	A 26044
4a	1	—CH_2CH_2—		A 33184
5a	1	—CH_2CH_2—		A 33183

Examples of suitable compounds conforming to the structure



are as follows:

TABLE II

Ex. No.	R	R'
1b	8–22 carbons	0 to 4 carbons.
2b	Aromatic	0 to 4 carbons.
3b	8–22 carbons	Aromatic.
4b	8 carbons	2 carbons.
5b	10 carbons	2 carbons.
6b	12 carbons	2 carbons.
7b	14 carbons	2 carbons.
8b	16 carbons	2 carbons.
9b	18 carbons	2 carbons.
10b	9 carbons	0 carbon.
11b	8 carbons	1 carbon.
12b	8 carbons	2 carbons.
13b	8 carbons	3 carbons.
14b	8 carbons	4 carbons.
15b		2 carbons.
16b	8 carbons	

In many instances our preference is to employ amidic acids in which the 2-carbonyl atoms are connected by a 2-carbon atom chain. This specific class has been suggested for use particularly in the form of salts in connection with certain petroleum lubricants. See U.S. Patent No. 2,604,449, dated July 22, 1952, to Bryant et al.

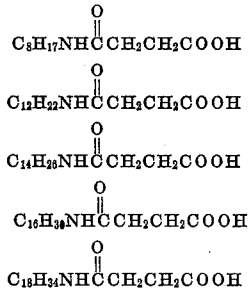
The products described in the above-mentioned patent may be derived from primary amines or secondary amines. Note the herein described products are obtained from primary amines only. The reaction is essentially that of a dibasic acid or anhydride with a primary amine.

Suitable amines which may be employed are mono-n-octylamine, mono-n-decylamine, mono-laurylamine, mono-myristylamine, mono-palmitylamine, mono-stearylamine, mono-linoleylamine, monooleylamine, etc. These amines as obtained in commerce may represent a mixture of amines. Such commercial mixture is perfectly satisfactory for the purpose. The acids or anhydrides which may be employed are any which yield a 2-carbon atom chain between the two carbonyl carbon atoms. The 2-carbon atom chain may be the ethylene groups or a substituted ethylene group such as in succinic acid, maleic acid, itaconic acid, etc. The preference is a matter of convenience and to assure maximum yield is to use the anhydride where available instead of the acid. The pro-

cedure employed in the manufacture is that described in aforementioned U.S. Patent No. 2,604,449, with particular reference to the following specific examples:

N-mono-n-octyl-itaconamic acid
N-mono-decyl-itaconamic acid
N-mono-lauryl-itaconamic acid
N-mono-myristyl-itaconamic acid
N-mono-palmityl-itaconamic acid
N-mono-stearyl-itaconamic acid

Typical examples which have been found particularly effective for the present purpose include

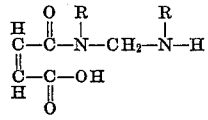


and a cocoamine product in which the amine is the mixed amine derived from coconut oil fatty acids.

PART 2

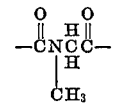
The use of high molal amines or polyamines as corrosion inhibitors is well known. A large variety have been used. Generally speaking, for obvious reasons they are surfactants.

By and large, if one examines those which appear to be closest in structure to the herein described products invariably they exhibit either one or more of three characteristics; (*a*) they contain at least one basic nitrogen atom; (*b*) they contain the carboxyl group present in the form of a salt; (*c*) they are amino acids, i.e., the amides of N-methyl glycine (sarcosine) which, of course, are essentially the amides of a high molal acid, and (*d*) they are essentially surface active. For instance, examples illustrating the above appear in U.S. Patent 2,699,427 dated January 11, 1955, to Smith et al. For instance, one of the corrosion inhibitors herein described is the following:



where *r* is lauryl.

The compounds herein described are differentiated from the N-acyl sarcosines by the fact that the linkage involving the two carbonyl carbons, one carbonyl carbon atom derived from methyl amino acetic acid, and the other from a high molal fatty acid, includes a nitrogen atom, thus:



They are differentiated from the compounds of the aforementioned amidic acids or salts of U.S. Patent 2,699,427 by the absence of a basic nitrogen atom.

The difference in structure is significant over and above being a differentiation in that the herein described amidic acids give corrosion inhibition under a variety of circumstances and are much more effective than products of the nearest comparable structure and is emphasized by the following tests:

Static test.—Both the hydrocarbon and water phases from a known corrosive source were used as a corrosive medium. These liquids were kept in well filled, stoppered

bottles during handling prior to their use in this test to prevent absorption of air. As a final precaution the fluids were purged for one hour with natural gas prior to use.

In testing the compositions, cleaned and numbered one pint bottles were purged with natural gas. The corrosive fluids were then placed in the bottles together with a measured amount of the compound under test. Weighed mild steel strips which had been cleaned by sand blasting were then placed in the corrosive liquids in such a way that the mid point of the test strip was approximately at the interfacial level. At all times precautions were taken to exclude air from the corroding system during charging.

The bottles containing the oil, brine and the test strips were allowed to stand 14 days at room temperature. At the end of this time the strips were removed, cleaned by carefully treating with 1% hydrochloric acid solution a few seconds, washing with water and finally with acetone. The dry strips were re-weighed to determine the weight loss. Blanks were run to provide a basis for comparison.

The changes in the weight of the test strips during the corrosion test were taken as a measurement of the inhibitor composition. Results are reported as a calculated protection percentage for each of the test strips taken from the inhibited fluids in accordance with the following formula:

$$\frac{L_1 - L_2}{L_1} \times 100 = \text{percent protection}$$

in which L_1 is the loss in weight of strips taken from the uninhibited fluids and L_2 is the loss in weight of the strips, taken from the inhibited fluid. Thus, if the blank loss were 100 mg. during the course of the test and the test strip subjected to fluids containing an inhibitor composition lost 5 mg. during the test, the protection would be reported as 95 percent.

Dynamic tests.—The effectiveness of the amidic acids as corrosion inhibitors may be better and more fully understood by reference to certain dynamic tests which have ben conducted. In the first of these tests ten percent sodium chloride containing 200 p.p.m. acetic acid was used as the aqueous phase and kerosene was used as the hydrocarbon phase. In conducting the test 400 ml. of the aqueous material and 100 ml. of the hydrocarbon were combined and heated to 150° to 155° F. with good agitation. At this point an iron coupon which had previously been cleaned by sand blasting was suspended in the moving liquid at a point below the normal interfacial level. At five minute intervals samples of the water were removed and the iron content was determined colorimetrically by means of the standard thiocyanate procedure. The rate of corrosion in the system is directly proportional to the increase in iron content of the water. By comparison of an inhibited and an uninhibited test it is found that the protection afforded by an inhibitor can be calculated to a percentage figure by the following formula:

$$\frac{\text{Fe (blank)} - \text{Fe (sample)}}{\text{Fe (blank)}} \times 100 = \text{percent protection}$$

In practice it has ben found advantageous to run two or more concentrations of inhibitor with one being high enough to show no detectable iron during the test period. The duration of the test is an arbitrary matter, but generally one half hour is considered sufficient for reliable results since in this period of time the iron content of the blank will reach a value of approximately 50 p.p.m. which will be high enough for accurate determination.

In the second dynamic tests 3% sodium chloride containing 500 p.p.m. acetic acid, saturated with carbon dioxide and kerosene are pumped into an agitated cell at a rate of 20 ml. per minute of brine and 10 ml. per minute of kerosene. The cell contains a sandblasted iron coupon measuring 1¼ x 3¼ inches. The gaseous corrosion products are passed through a thermal conductivity cell

to determine the amount of hydrogen evolved from the corrosion process.

In conducting this test a blank corrosion rate is first established followed by the injection of an inhibitor in sufficient concentration to establish a rate of hydrogen evaluation of 10% or less of the blank determination. This point will represent 90% or above protection. The inhibitor stream is then replaced by the original corrosive liquids and the persistence of the film formed during inhibition is observed. By plotting the rate of hydrogen evaluation against time an inhibition curve can be drawn which will correspond closely to the action of a material under natural corrosive conditions.

PART 3

The herein described products are used as corrosion inhibitors in the same manner as conventionally available corrosion inhibitors. Such procedure has been described in one or more of the patents referred to, to wit, U.S. Patents Nos. 2,736,658, dated February 28, 1956, to Pfohl et al.; 2,756,211, dated July 24, 1956, and 2,727,003 dated December 13, 1955, both to Hughes, and Re. 23,227, dated May 9, 1950, to Blair et al.

In one way the herein described corrosion inhibitors show some variation from a variety of commonly used corrosion inhibitors insofar that their solubility in organic solvents is somewhat different, for instance, they are not appreciably soluble in some of the more common solvents, such as mineral spirits, xylene, etc.

In many cases being more effective a comparatively dilute solution can be used, for example, a solution in low molecular weight alcohols. Examples of such solutions are the following:

Example 1d

$C_8H_{17}NHCCH_2CH_2COOH$ (O)

ten parts by weight, methyl alcohol 90 parts by weight.

Example 2d

$C_{12}H_{22}NHCCH_2CH_2COOH$ (O)

ten parts by weight, methyl alcohol 25 parts by weight, xylene 65 parts by weight.

Example 3d

$C_{14}H_{26}NHCCH_2CH_2COOH$ (O)

ten parts by weight, methyl alcohol 25 parts by weight, xylene 65 parts by weight.

Example 4d

$C_{16}H_{30}NHCCH_2CH_2COOH$ (O)

ten parts by weight, isopropyl alcohol 90 parts by weight.

Basically, the herein described corrosion inhibitors have at least 2 distinct advantages over the nearest compounds which show a somewhat related structure and have been referred to previously, i.e., the amides of N-methyl glycine (sarcosine).

In the first place, compounds of the kind herein described can be made at considerably less expense than the corresponding N-acyl sarcosines. Such products are made by the use of chloroacetic acid and methyl amine, followed by a reaction involving a fatty acid chloride. The products herein described can be obtained from commercially available higher fatty acid amines, and succinic anhydride of technical purity. It is estimated that in a general way the products herein described can be produced at approximately two-thirds the cost involved in the production of N-acyl sarcosines in which the same fatty acid radical appears.

Secondly, in many instances there is a very significant and definite advantage in the herein described corrosion inhibitors over and above the lower cost of preparation.

The following tables show the results of static room temperature tests made on the amido acid type corrosion inhibitors as compared to the N-acyl sarcosine. This study was made using two corrosive hydrocarbon streams and a synthetic mixture of kerosene, sodium chloride and a wetting agent. Table III shows the results of tests using fluids from the Live Oak Field:

TABLE III

Inhibitor	Structure	Protection	
N-acyl sarcosine—Type A.	N-lauryl sarcosine	79.8	80.0
N-acyl sarcosine—Type B.	N-oleyl sarcosine	77.6	74.3
N-acyl sarcosine—Type C.	N-stearyl sarcosine	67.1	------
A-33032	$C_8H_{17}NHCCH_2CH_2COOH$ (O)	98.7	------
A-33031	$C_{12}H_{22}NHCCH_2CH_2COOH$ (O)	99.6	------
A-33047	$C_{14}H_{26}NHCCH_2CH_2COOH$ (O)	98.5	------
A-33044	$C_{16}H_{30}NHCCH_2CH_2COOH$ (O)	98.0	------
A-26034	$C_{18}H_{34}NHCCH_2CH_2COOH$ (O)	88.4	------
A-26044	Cocoamine product	99.1	98.4

A direct comparison between A–33031 and N-acyl sarcosine Type and A–26034 and N-acyl sarcosine Type C shows the N-acyl sarcosines to be much less effective in this medium.

Table IV shows tests run in American Bitumuls and Asphalt Company naphtha:

TABLE IV

Inhibitor	Percent Protection	
N-acyl sarcosine—Type A	37.0	37.2
N-acyl sarcosine—Type B	38.4	----------
N-acyl sarcosine—Type C	22.8	----------
A–26044	95.0	95.5
A–33031	98.8	----------
A–33044	79.8	----------
A–33032	90.7	----------

Table V shows the results obtained in a test in which the contact angle of the kerosene was controlled to a point about 90° by the addition of an oxyethylated red oil amide in which 5 moles of ethylene oxide have been added per oleyl amide molecule. The object of this test was to eliminate the variation in the wetting characteristics imparted by the various compounds. The test is one of efficiency under standardized conditions. This technique is considered sound and the results are more reliable than those obtained without control of this factor.

TABLE V

Inhibitor:	Percent protection
N-acyl sarcosine—Type A	98.6
N-acyl sarcosine—Type C	72.9
A–33031	98.2
A–26034	84.3
A–26044	97.8
Oxyethylated [1] red oil amide above described	0.2

[1] Used at 100 p.p.m. in all samples.

Table V probably represents a realistic evaluation of these compounds since the factor of wetting has been minimized in these tests.

The unexpected high specificity of the herein described

corrosion inhibitors is emphasized by the following fact. Certain compounds, to wit,

$$RCON(CH_3)CH_2COOH$$

have a structure which superficially appears to be somewhat similar or somewhat analogous. However, when members of this class of compound are employed for corrosion inhibition in the manner in which the products of the present invention are effective one finds the results are unexpectedly inferior. Reference is made to Table VI which illustrates this.

Table VI shows the results obtained in the first of the described dynamic tests in which iron determinations were made on the brine from the corroding system. The duration of these tests was one hour.

TABLE VI

Inhibitor	Percent Protection	
	10 p.p.m.	20 p.p.m.
A-33038	87	99
A-33032	89	99
A-33044	95	99
A-33184	86	99
A-33183	84	98
N-acyl sarcosine—Type A	79	97
N-acyl sarcosine—Type B	81	96
N-acyl sarcosine—Type C	79	91

The table following (Table VII) shows the results obtained in the second dynamic tests.

TABLE VII

[Dynamic test measuring hydrogen evolved. 3% NaCl brine, 500 p.p.m. acetic acid saturated with CO_2, kerosene, temperature 160±2° F.]

Time, Hours	Inhibitor	p.p.m. Inhibitor	Hydrogen Units	Percent Protection	Remarks
1	None	0	41	0	Blank.
1	A-26044	100	2	95.0	
7	None	0	2	95.0	Film life.
1	None	0	41	0	Blank.
1	A-33032	100	3	92.7	
3	None	0	3	92.7	Film life.
1	None	0	41	0	Blank.
1	A-33038	100	4	90	
2	None	0	4	90	Film life.

Incidentally, it is well known that compounds of the kind herein described when derived from an unsaturated succinic acid such as commercial C_{10}–C_{12} alkenyl succinic acid are effective as additives to lubricating oils and the like. See U.S. Patent 2,490,744, dated December 6, 1949, to Trigg et al. It is to be noted that the present invention is concerned with inhibiting corrosion of corrodible ferrous metals employed in the recovery, transportation and refining of petroleum hydrocarbons, i.e., the unrefined products or those transported by pipelines, and not with the specific problems encountered in lubricating oils. However, the differentiation is not based on the class of materials with which the processes or compositions are concerned but rather with the results which are obtainable by means of succinic acid as a reactant in comparison with the results obtained with an alkenyl succinic acid as a reactant. This is illustrated in the following table:

TABLE VIII

Inhibitor	Composition	Percent Protection	
		10 p.p.m.	20 p.p.m.
AA	Armeen 8 plus trilsobutenyl succinic anhydride.	0	1
BB	Armeen 8 plus succinic anhydride	89	99

In using these improved compositions for protecting oil or gas producing equipment which comes in contact with corrosive materials, excellent results may be obtained by injecting an appropriate quantity of a selected composition into the producing well so that it may mingle with the produced fluids and come in contact with the casing, tubing, pumps and other producing equipment. It may, for example, be introduced as a solution in a suitable solvent into the top of the casing, thus causing it to flow down the annular space and thence back through the tubing, etc. In general it has been found that this procedure suffices to inhibit corrosion throughout the entire system of production, and collection, even including field tankage.

It should be pointed out that the corrosiveness of produced or transported fluids will vary greatly from one environment to another and the proportion of corrosion inhibiting agent required to protect effectively each system will vary also. Thus, it may be possible to control effectively the corrosion in some systems by the addition of as little as 10 p.p.m. of one of the described compositions while in other systems it may be necessary to add 200 p.p.m. or more.

It may be desirable to convert these new compositions into solid sticks by use of wax or other solid materials. Such sticks can be applied to gas condensate wells by means of special fittings at the well heads which will allow the solid stick to reach the bottom of the well, then dissolve slowly, releasing the inhibitor into the producing stream over a period of time.

When applying these new compositions to gas pipelines it is desirable to meter a measured quantity of the selected inhibitor, as a solution, into the pipeline. The amount used will depend upon the volume being transported by the line and by the nature of that liquid. It is advisable to overtreat the line at first and gradually reduce the quantity of inhibitor to an efficient use concentration.

It is to be understood that the improved compositions may be used alone, but are not limited to use alone and may be employed along with other agents commonly introduced into the described corrosive situations for breaking emulsions, limiting scale formation, etc. It is further evident that the improved compositions are not restricted to use in the described systems but may be employed to perform this function in other places such as tankers, refineries, storage tanks, or other places where corrosive brines may be met whether these brines are of naturally occurring origin or not.

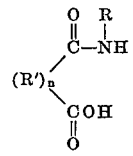
The usefulness of these improved compositions is further demonstrated by tests which have been described in U.S. Patent No. 2,466,517, dated April 5, 1949, to Blair et al., column 8, lines 15 to 45. Using the technique described in the patent with the exception that a 25% solution of A–26044 in xylene and methanol was substituted for the described imidazoline, results which were substantially better were obtained in that protection figures at more than 90% were found possible with one-third less inhibitor.

Similarly, when the product described as A–26044 was converted into stick form by use of a high melting wax and stearyl alcohol and weighted with barium sulfate as described in the aforementioned patent, it could be applied as described in U.S. Patent No. 2,466,517, column 8, lines 45 and following. However, similar protection figures were possible using 0.4 pound of active material per stick. This represents a saving of 33%.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent, is:

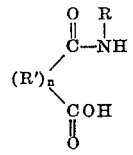
1. A method of inhibiting corrosion of corrodible ferrous metals employed in the recovery, transportation and refining of petroleum hydrocarbon fluids; said hydrocarbon fluids containing water and a member of the group of corrosive materials consisting of hydrogen sulfide, carbon dioxide, organic acids containing 2 to 4 carbon atoms per molecule, combinations of these materials with oxygen, and combinations of said materials with each other and oxygen; said method comprising adding

to said fluids at least 5 parts per million of a non-basic amidic acid of the formula:



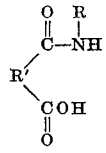
in which R represents a member of the class of aliphatic, aryl and alicyclic hydrocarbon radicals having 6 to 22 carbon atoms, R′ represents a member of the class of aliphatic alicyclic and aryl hydrocarbon radicals having not over 6 carbon atoms, and *n* represents a numeral not greater than one and including zero.

2. A method for reducing the corrosiveness to corrodible ferrous metal of the corrosive petroliferous well fluid including moisture and hydrogen sulfide; said method comprising adding to said fluids a non-basic amidic acid having the formula:



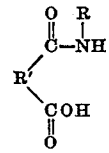
in which R represents a member of the class of aliphatic, aryl and alicyclic hydrocarbon radicals having 6 to 22 carbon atoms, R′ represents a member of the class of aliphatic, alicyclic and aryl hydrocarbon radicals having not over 6 carbon atoms, the carbonyl carbon atoms being separated by not more than 4 carbon atoms, and *n* represents a numeral not greater than one and including zero.

3. A method for reducing the corrosiveness to corrodible ferrous metal of the corrosive petroliferous well fluid including moisture and hydrogen sulfide; said method comprising adding to said fluids a non-basic amidic acid having the formula:



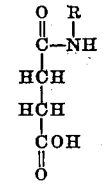
in which R represents a member of the class of aliphatic, aryl and alicyclic hydrocarbon radicals having 6 to 22 carbon atoms, and R′ represents a member of the class of aliphatic, alicyclic and aryl hydrocarbon radicals having not over 6 carbon atoms, the carbonyl carbon atoms being separated by not more than 2 carbon atoms.

4. A method for reducing the corrosiveness to corrodible ferrous metal of the corrosive petroliferous well fluid including moisture and hydrogen sulfide; said method comprising adding to said fluids a non-basic amidic acid having the formula:



in which R represents an aliphatic hydrocarbon radical having 6 to 22 carbon atoms, and R′ represents an aliphatic hydrocarbon radical having not over 6 carbon atoms, the carbonyl carbon atoms being separated by not more than two carbon atoms.

5. A method for reducing the corrosiveness to corrodible ferrous metal of the corrosive petroliferous well fluid including moisture and hydrogen sulfide; said method comprising adding to said fluids at least 5 parts per million of a non-basic amidic acid having the formula:



in which R represents the radical of a higher fatty acid having at least 8 and not over 22 carbon atoms.

6. The method of claim 5 in which R is a fatty acid radical having 10 carbon atoms.

7. The method of claim 5 in which R is a fatty acid radical having 12 carbon atoms.

8. The method of claim 5 in which R is a fatty acid radical having 14 carbon atoms.

9. The method of claim 5 in which R is a fatty acid radical having 16 carbon atoms.

10. The method of claim 5 in which R is a fatty acid radical having 18 carbon atoms.

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