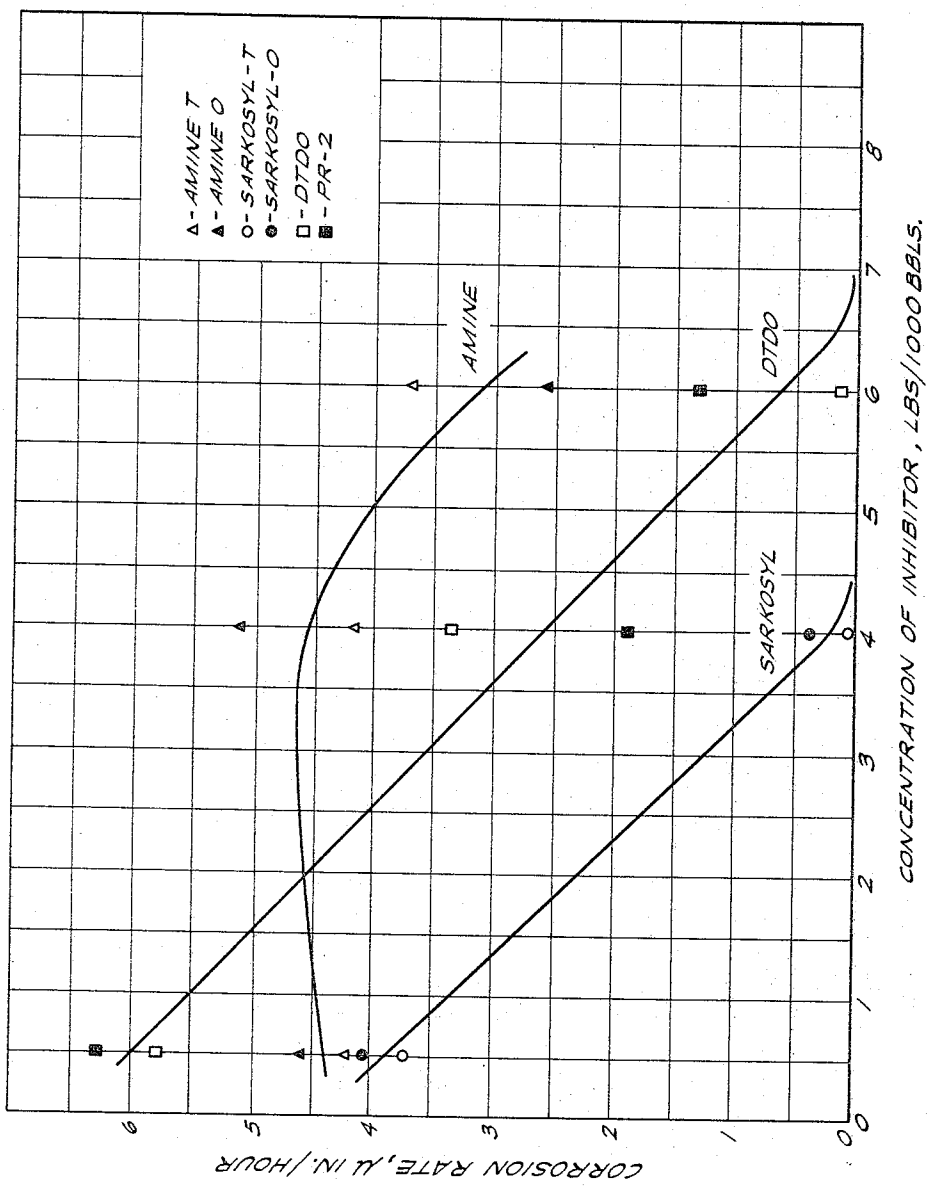
Aug. 22, 1967 R. L. LITTLER ETAL 3,337,472

COMPOSITION FOR INHIBITING CORROSION

Filed April 8, 1966



INVENTORS
ROBERT L. LITTLER
GLENN A. MARSH
EDWARD SCHASCHL
BY William S. Brown
ATTORNEY

United States Patent Office 3,337,472 Patented Aug. 22, 1967

3,337,472

COMPOSITION FOR INHIBITING CORROSION

Robert L. Littler, Bay City, Tex., and Glenn A. Marsh and Edward Schaschl, Fullerton, Calif., assignors to Union Oil Company of California, Los Angeles, Calif., a corporation of California

Filed Apr. 8, 1966, Ser. No. 541,376
4 Claims. (Cl. 252—392)

This application is a continuation-in-part of application Serial No. 400,269, filed Sept. 29, 1964, which is in turn a continuation-in-part of application Ser. No. 243,657, filed Dec. 10, 1962, both applications abandoned.

This invention relates to a corrosion inhibiting composition and more particularly to the inhibition of corrosion of ferrous metals contacted by petroleum fractions.

Petroleum fractions such as gasoline, diesel fuel, and naphthas are often seriously corrosive to ferrous metal structures such as storage tanks, pipelines, earth well bore tubing and casing, processing equipment, etc. Corrosion of such structures is inhibited by incorporating in the petroleum fraction a small amount of a corrosion inhibitor before entry of the fraction into the metal structure. The inhibitor selected, aside from having no deleterious effect upon the petroleum fraction itself or its use, must, in the amount in which it is used, reduce corrosion in the equipment to a tolerable level. Hence, the cost of the inhibitor, considered in the light of the amount in which it is used per volume of petroleum fraction, should be as low as possible.

Numerous excellent corrosion inhibitors are known, which, when used in petroleum fractions, will reduce the corrosion of ferrous structures to a very low level. Unfortunately, the cost of such inhibitors is very great. Other, less expensive inhibitors, are less effective per unit of inhibitor employed, and therefore must be used in undesirably great amounts.

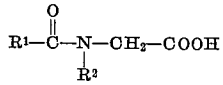
It is an object of this invention to provide a new inhibitor composition which provides excellent corrosion protection at reasonable cost.

Another object of this invention is to provide an improved method for inhibiting the corrosion of various types of ferrous metal equipment.

The figure is a graph prepared from corrosion rates experimentally determined using individual components of the composition forming the subject matter of this invention.

The objects of this invention are accomplished by incorporating in the petroleum fraction which is to be stored or transported by the equipment and which is corrosive to ferrous metals, a small amount, in the range of about 5 to 50 parts per million, and preferably about 5 to 15 parts per million of the corrosion-inhibiting composition of this invention which comprises a combination of at least two of the following components: (1) an acyl derivative of N-alkyl amino acetic acid, (2) a substituted imidazoline, and (3) a fatty acid addition salt of a diamine.

The acyl derivative of N-alkyl amino acetic acid has the formula:



in which R^1 is an aliphatic radical of about 10 to 24 carbon atoms, and R^2 is hydrogen or an alkyl radical of 1 to about 6 carbon atoms. Preferred compounds are those in which R^2 is a methyl group, that is, those compounds that are derivatives of methylamino acetic acid. More especially preferred are compounds wherein the R^1 group

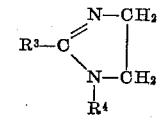
is a fatty acid residue and is derived from tall oil or oleic acid.

Since it is difficult and expensive to obtain compounds of the above formula in pure form, this invention contemplates the use of mixtures of such compounds. The composition of such mixtures may range from those in which the fatty acid residue (R^1) is 95% C_{12} to compounds in which 80% of the fatty acid residue is derived from C_{18} or higher acids. The following specific compounds are illustrative:

(N-oleoyl) methylamino acetic acid
(N-palmitoleoyl) methylamino acetic acid
(N-dodecylenoyl) methylamino cetic acid
(N-ricinoleoyl) methylamino acetic acid
(N-dicylenoyl) methylamino acetic acid
(N-linolenoyl) methylamino acetic acid
(N-lauroyl) methylamino acetic acid
(N-palmitoyl) methylamino acetic acid
(N-stearoyl) methylamino acetic acid

Other compounds are the corresponding acids wherein the R^2 radical is hydrogen or an ethyl, propyl, butyl, amyl, or hexyl radical.

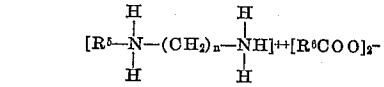
The substituted imidazoline has the formula:



in which R^3 is an aliphatic or cycloaliphatic radical of about 10 to 32 carbon atoms and R^4 is an alkyl, a hydroxy-substituted alkyl, or an amino-substituted alkyl radical of about 1 to 6 carbon atoms. Preferred compounds are those where R^4 is 2-hydroxyethyl and R^3 is either heptadecenyl or the residue from tall oil fatty acids. Other suitable compounds are:

2-heptadecenyl-1-(4-hydroxybutylimidazoline)
2-dodecyl-1-(5-hydroxypentylimidazoline)
2-(3-cyclohexylpropyl)-1-(2-hydroxyethylimidazoline)
2-dodecylcyclohexyl-1-(2-hydroxyethylimidazoline)
2-octadecyl-1-(3-hydroxypropylimidazoline)
2-heptadecenyl-1-methylimidazoline
2-heptadecenyl-1-ethylimidazoline
2-heptadecenyl-1-butylimidazoline
2-dodecyl-1-pentylimidazoline
2-(3-cyclohexylpropyl)-1-methylimidazoline
2-dodecylcyclohexyl-1-ethylimidazoline
2-octadecyl-1-propylimidazoline
2-heptadecenyl-1-(2-aminoethylimidazoline)
2-tridecyl-1-(2-aminoethylimidazoline)
2-pentadecyl-1-(2-aminoethylimidazoline)

The fatty acid salt of a diamine has the formula:



in which R^5 and R^6 are aliphatic radicals of about 10 to 32 carbon atoms per radical and n is an integer from 1 to about 4. Preferred compounds are those in which n is 3, R^5 is either oleyl or is derived from tallow acids and consists mainly of C_{16} and C_{18} normal, saturated hydrocarbon chains and C_{18} monounsaturated chains, and R^6 is oleyl or is derived from tall oil acids free of resin acids. Examples of other suitable compounds are octadecenylaminopropyl ammonium oleate, octadecenylaminobutyl ammonium oleate, octadecenylaminoethyl ammonium oleate, octadecenylaminopropyl ammonium stearate, octadecenylaminopropyl ammonium palmitate, octadecenylaminoethyl ammonium laurate, hexadecenylaminopropyl ammonium oleate, dodecenylaminopropyl

ammonium oleate, and mixtures of the foregoing compounds.

The effectiveness of the compositions of this invention is demonstrated by experimental tests which show the corrosion rates for metal specimens when protected by the compositions of the invention and when protected by the individual constituents of the composition when used alone. A mild steel coupon, initially 5 mils thick, is etched for 15 seconds in 6 N hydrochloric acid containing 1% iron chloride. Then the coupon is prerusted by alternate dipping into a rusting solution for 10 seconds, with intermittent drying, for 4 complete cycles. The rusting solution is an aqueous 3% sodium chloride, 1% iron chloride solution. A uniform yellow-orange rust that penetrates to 10 to 15 microinches is produced on the coupon.

The prerusted coupon is inserted in a 1-quart narrow-mouthed square bottle containing 450 milliliters of isooctane and 450 milliliters of aerated 3% brine. The coupon is kept in the hydrocarbon phase (which contains the inhibitor to be tested) for a soaking period of 1 hour. After this the bottle is oscillated at a rate of 2 cycles per minute to immerse the coupon alternately in the 2 phases. Metal loss measurements are made throughout the test by electronic means that do not interfere with the continuity of the test. The average slope of the corrosion curve for duplicate runs is taken as the corrosion rate. Since the curves are not precisely linear, the slope is chosen between fixed time limits of 40 and 60 hours after the start of the test. A good inhibitor permits only a low corrosion rate—and in some cases no corrosion—while a poor inhibitor or too little inhibitor permits a rate approaching or perhaps exceeding the blank (no inhibitor) rate of metal loss per hour.

Example

The results of experiments performed according to the above procedure are set forth in Table I. Blanks were run to determine corrosion rate in the absence of any inhibitor. This was found to be 5.50 microinches per hour. In Table I trade names, defined as follows, are used for purpose of brevity.

Sarkosyl O—(N-oleoyl) methylamino acetic acid.

Sarkosyl T—N-(tall oil-derived acyl) methylamino acetic acid.

Amine O—2 - heptadecenyl - 1-(2-hydroxyethylimidazoline).

Amine T—2 - (tail oil-derived)-1-(2-hydroxyethylimidazoline).

DTDO—[R—N(H)—CH_2—CH_2—CH_2—N(H)H]$^{++}$[$C_{17}H_{33}CO]_2^-$

in which R is derived from tallow acids and consists mainly of C_{16} and C_{18} normal, saturated chains and C_{18} mono-unsaturated chains.

PR–2—Same as DTDO except R is an oleyl group and the acid radical is derived from tall oil acids free of resin acids.

TABLE I

Components Concentration [1] and Individual Corrosion Rates						Corrosion Rate of Combined Components	Percent Protection [2] of Individual Components			Percent Protection		Cost of Treatment,[3] $ per 4 lb. Treatment
Component 1	Corrosion Rate, μin./hr.	Component 2	Corrosion Rate, μin./hr.	Component 3	Corrosion Rate, μin./hr.		Component 1	Component 2	Component 3	Sum of Individual Components	Combined Components	
Sarkosyl T 0.5 lb.	3.9	Amine T 0.5 lb.	4.4	DTDO 3.0 lb.	3.5	0.08	29	20	26	75	99	1.92
Sarkosyl T 0.5 lb.	3.9	Amine T 0.5 lb.	4.4	PR–2 3.0 lb.	3.5	0.07	29	20	26	75	99	1.92
Sarkosyl O 0.5 lb.	3.9	Amine O 0.5 lb.	4.4	PR–2 3.0 lb.	3.5	0.05	29	20	26	75	99	1.95
Sarkosyl T 2.0 lb.	2.3	Amine T 2.0 lb.	4.6			0.13	58	16		74	98	2.86
Sarkosyl O 1.0 lb.	3.3			PR–2 3.0 lb.	3.5	0.15	40		26	66	97	2.20
Sarkosyl O 1.0 lb.	3.3	Amine O 3.0 lb.	4.7			0.05	40	15		55	99	2.50
Sarkosyl O 2.0 lb.	2.3			PR–2 2.0 lb.	4.6	0.25	58		16	74	95	2.80
		Amine O 2.0 lb.	4.6	PR–2 2.0 lb.	4.6	0.75		16	16	32	86	1.76
Sarkosyl O 2.0 lb.	2.3	Amine O 2.0 lb.	4.6			0.20	58	16		74	96	3.00

[1] In pounds per thousand barrels of isooctane.

[2] Percent Protection=100 $\left(1-\frac{\text{Corrosion Rate}}{\text{Blank Rate}}\right)$.

[3] Cost based on less than 10 drum quantities: Sarkosyl O, 1.00/lb.; Sarkosyl T, 0.95/lb.; Amine O, 0.50/lb.; Amine T, 0.48/lb.; DTDO, 0.40/lb.; PR–2, 0.40/lb.

In evaluating the results of the foregoing experiments, it should be borne in mind that while the acyl derivatives of methylamino acetic acid tested prove to be extremely effective as corrosion inhibitors when used alone, these materials are too costly at the levels required to provide adequate corrosion protection. The imidazoline and fatty acid amine salt additives are very much less expensive, but these materials, by themselves, do not provide an adequate level of corrosion protection unless used in large amounts. It is seen, nevertheless, that the combination of a very small amount of the derivative of N-alkylamino acetic acid, together with an equal amount of the imidazoline and a greater amount of the fatty acid salt (the least expensive additive), provides, at a reasonable total dosage level of 4 pounds per thousand barrels, a very adequate level of corrosion protection at low cost.

The graphs shown in the drawing were prepared by experimentally determining corrosion rates, in accordance with the method described above, using individual components of the claimed composition in different amounts. For example, corrosion rate in microinches per hour was determined for both Amine T and Amine O at doses of 0.5, 4.0 and 6.0 pounds per 1,000 barrels of isooctane. From the curve it is apparent that even at the 6 pound dosage, Amine T and Amine O were not particularly effective. On the other hand, while Sarkosyl O and T are not very effective at 0.5 pound dosage, they give substantially complete protection at 4.0 dosage. DTDO and PR–2 appear to have negative action at 0.5 pound dosage but give substantially complete protection at a dosage between 6 and 7 pounds.

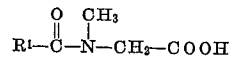
Best results are obtained by mixing together at least one compound of each of the three components; however, substantially improved corrosion at lower cost can be obtained by mixing together two components in the amounts of about 1 to 3 parts of one with 3 to 1 parts of the other. For example, as shown in Table I, Sarkosyl O and Amine T give almost complete protection at a lower cost than Sarkosyl T alone. The same is true of the combination of Sarkosyl O and PR–2. Amine O together with PR–2 give a substantial measure of protection at a low cost. But the combination of the three components consistently gives the greatest protection against corrosion at the lowest cost. Regardless of whether two or three components are mixed together, each component should be present in an amount not less than about 10 percent by weight of the mixture, i.e., a range of about 10 percent to about 90 percent by weight, and where two components are used, each should be present in an amount of at least 25 percent by weight. In order to reduce the cost of inhibiting, the acyl derivative of N-alkyl amino acetic acid should be kept as low as possible consistent with adequate corrosion protection. Proportions of about 0.8 to 1.2 parts by weight for each of the N-alkyl amino acetic acid derivative and the imidazoline and about 5.5 to 6.5 parts by weight for the diamine salt have been found to give particularly good results.

Although the compounds and proportions shown in the above example have been found to give optimum results, the synergistic effect of applicants' compositions is not limited to the specific compounds and proportions set forth therein. Compositions comprising a wide variety of compounds, as set forth in the above generic formulae, and proportions as set forth in the preceding paragraph (at least about 10 percent of each component) will exhibit synergism comparable to that shown in the examples.

We claim:

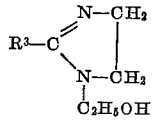
1. A corrosion inhibiting composition consisting of the following three components:

(I) About 0.5 part by weight of an acyl derivative of N-alkyl amino acetic acid of the formula:



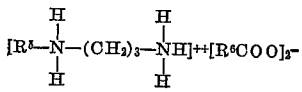
in which R^1 is selected from the group consisting of N-oleoyl and N-(tall oil-derived acyl);

(II) About 0.5 part by weight of an imidazoline of the formula:



in which R^3 is selected from the group consisting of 2-heptadecenyl and 2-(tall oil-derived); and

(III) About 3 parts by weight of a fatty acid salt of a diamine of the formula:

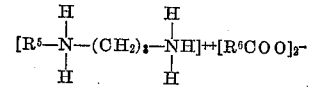


in which R^5 is selected from the group consisting of: (a) Tallow derived acids of mainly C_{16} and C_{18} normal, saturated chains and C_{18} mono-unsaturated chains, and (b) an oleoyl group; and R^6 is selected from the group consisting of: (a) $C_{17}H_{33}$ and (b) tall oil derived acids free of resin acids.

2. A corrosion inhibiting composition consisting of:

(a) about one part by weight of a compound selected from the group consisting of an N-(oleoyl) methyl amino acetic acid, and N-(tall oil-derived acyl) methyl amino acetic acid; and

(b) about three parts by weight of a fatty acid salt of a diamine of the formula:



where R^5 is selected from the group consisting of oleoyl and tallow acids having mainly C_{16} and C_{18} normal saturated hydrocarbon chains and C_{18} mono unsaturated hydrocarbon chains; and R^6 is selected from the group consisting of tall oil acids free of resin acids and $C_{17}H_{33}$.

3. A corrosion inhibiting composition consisting of:

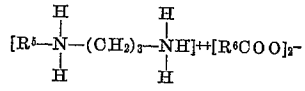
(a) about one part by weight of a compound from the group consisting of: an N-(oleoyl) methyl amino acetic acid; and N-(tall oil-derived acyl) methyl amino acetic; and

(b) about three parts by weight of a compound from the group consisting of: 2-heptadecenyl-1-(2-hydroxyethyl)imidazoline; and 2-(tall oil-derived)-1-(2-hydroxyethyl)imidazoline.

4. A corrosion inhibiting composition consisting of about equal parts by weight of:

(a) 2-heptadecenyl-1-(2-hydroxyethyl)imidazoline; and

(b) a fatty acid salt of a diamine of the formula:



were R^5 is an oleoyl group and R^6 is derived from tall oil acids free of resin acids.

References Cited

UNITED STATES PATENTS

2,468,163	4/1949	Blair et al.	252—8.55
2,736,658	2/1956	Pjohl	44—66 X
2,790,779	4/1957	Spevack et al.	252—392
2,945,821	7/1960	Sterlin	252—392
3,034,907	5/1962	Kleeman et al.	252—392 X
3,116,252	12/1963	Beretvas	252—392 X
3,119,447	1/1964	Raifsnider et al.	252—389 X
3,201,411	8/1965	Freedman	252—8.55

LEON D. ROSDOL, *Primary Examiner.*

SAMUEL H. BLECH, *Examiner.*

M. WEINBLATT, *Assistant Examiner.*