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REACTION PRODUCTS OF IMIDAZOLINES AND ALKYLENE IMINODIACETIC ACIDS

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4 Claims. (Cl. 260—309.6)

This application is a division of my co-pending application Serial No. 825,401, filed July 7, 1959, now U.S. Patent No. 3,060,007 which application is a continuation-in-part of my application Serial No. 614,347, filed October 8, 1956, now abandoned.

This invention relates to novel corrosion and/or rust inhibitors particularly adapted for use in preventing corrosion of metals, especially iron, steel and ferrous alloys, by liquids containing corrosive compounds associated with oleaginous materials, such as petroleum oil, and to the method of preventing such corrosion.

The corrosion inhibitors of this invention find special utility in the prevention of corrosion of pipe and/or other equipment which is in contact with a corrosive oil-containing medium, as, for example, in oil wells producing corrosive oil or oil-brine mixtures, in refinery equipment, and in equipment used in the transportation of petroleum products such as tanks, drums, and pipe lines. The inhibitors of the present invention can be effectively employed in other systems or applications where it is desired to impart to ferrous metals resistance to attack by corrosive agents such as brine, weak inorganic acids, organic acids, CO_2, H_2S, etc. which may be associated with oleaginous materials such as petroleum oil.

The rusting of steel used in the transportation and storage of petroleum products has always presented a serious problem. The rusting of pipe lines and tanks used to transport petroleum light oil products represents per se a substantial annual economic loss in maintenance and replacement costs. In addition, the presence of sediment and rust as a result of corrosion and carry-over into fuel burning installation creates fuel quality and operating problems. The situation is particularly acute in the case of aviation gasoline where the hazard of engine stoppage through clogging of filters and carburetion equipment presents special hazards, but applies to the handling and use of motor and diesel fuels as well. The rusting of storage tanks used to supply industrial and household oil burner installations presents serious problems. In addition to the possibility of the storage tank rusting through, there is the danger that filters and fuel lines may become clogged, causing operating failure of the burner.

The problem of corrosion by rusting is associated with the presence of moisture in the oil products caused by entrainment, condensation and solution. In most cases, the problem is accentuated by the presence of a separate water phase. Thus, in the storage and bulk shipment of light products such as gasoline, it is common practice to maintain a water layer as tank bottoms. Even where a water layer is not used as tank bottoms, a separate water phase may form by repeated condensation of moisture, associated with tank breathing or the alternate expansion and contraction of the bulk with temperature changes, unless special precautions are taken. The problem of complete protection against rusting, therefore, requires prevention of rusting by metal surfaces exposed to both oil and water phases, and hence it is an object of my invention to provide a rust inhibitor which has the capacity of imparting protection against rusting in both phases.

Many types of oil soluble compounds are known to possess anti-rust properties. Among the most effective are organic acids, particularly fatty acids and derivatives thereof, organic acids of phosphorus and sulfur, as well as esters and amine or amide salts thereof. In general, materials of this type provide reasonably successful protection against rusting of metal surfaces exposed to an oil phase. Protection against rusting in the water phase, however, for the most part is lacking or is seriously deficient.

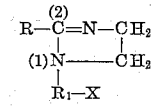
It is an object of the present invention to provide a corrosion and/or rust inhibitor adapted for use in preventing the corrosion and/or rusting of metals by liquids containing corrosive compounds associated with oleaginous materials, such as petroleum oils. Another object of the invention is to provide a method of preventing the corrosion and/or rusting of metals, especially ferrous metals, by liquids containing corrosive compounds associated with oleaginous materials, such as petroleum oils.

It is an object of this invention to provide a normally liquid non-lubricating hydrocarbon oil composition having improved rust inhibiting properties for the protection of metal surfaces of oil storage and/or handling equipment, whether exposed to the oil or to the water phase. Another object of the invention is to provide a normally liquid motor fuel and fuel oil composition which will inhibit the rusting and/or corrosion of metal surfaces of storage and/or handling equipment for such fuel. Other objects and advantages of the invention will become apparent from the following description thereof.

The foregoing objects can be attained by incorporating in the oleaginous material, such as petroleum oil, or a hydrocarbon oil fraction, for example a normally liquid, non-lubricating hydrocarbon oil fraction, such as gasoline or fuel oil, from about 0.0005% to about 0.01%, by weight, of the reaction product of a 1,2-disubstituted imidazoline and a substituted alkylene iminodiacetic acid having the general formula $RN[(CH_2)_xCOOH]_2$ in which R is an n-acyl radical or an n-alkyl radical containing from about 8 to about 30 carbon atoms, and preferably from about 12 to about 20 carbon atoms, and x is an integer of 1 to 3 inclusive.

The inhibitor of this invention is prepared by reacting 1:1 molar proportions of the imidazoline and substituted iminodiacetic acid, in a suitable solvent, at a temperature of from about room temperature (70–75° F.) to about 200° F., and preferably from about 150° F. to about 160° F., with intermittent agitation until the reactants are dissolved and the mixture than cooled to a temperature of from about 60° F. to about 80° F. If desired, the resultant product can be centrifuged or filtered to remove small amounts, if any, of insoluble matter. Any inert solvent such as isopropyl alcohol, n-butyl alcohol, kerosene, xylene, naphtha, etc. can be used, although it is preferred to use a mixture of 30% to 40%, by weight, n-butyl alcohol in xylene, or a 50% to 70% (vol.) solution of isopropyl alcohol in water.

The 1-2-disubstituted imidazolines used in the invention are of a type well known in the art, for example, such as are described in U.S. Patent 2,214,152 to Wilkes. Suitable imidazolines are the 1-2-disubstituted imidazolines having the general formula



in which R is an aliphatic group containing from about 8 to about 20 carbon atoms, R_1 is hydrogen or an aliphatic radical of not more than 6 carbon atoms, and X is a polar group such as a hydroxy or an amino radical. Examples of useful imidazolines includes 1-hydroxyethyl 2-

heptadecenyl imidazoline, 1-aminoethyl 2-undecyl imidazoline, 1-hydroxyethyl, 2-pentadecyl imidazoline, 1-aminoethyl 2-heptadecenyl imidazoline, 1-aminoethyl 2-heptadecyl imidazoline, 1- hydroxyethyl 2-heptadecyl imidazoline, 1-aminoethylethylimino 2-heptadecenyl imidazoline, and the like.

Examples of iminodiacetic acids suitable for use in the present invention are n-lauroyl-iminodiacetic acid, n-decyl iminodiacetic acid, myristoyl iminodiacetic acid, stearoyl iminodiacetic acid, n-hexadecanoyl iminodiacetic acid, n-octyl iminodiacetic acid, n-lauryl iminodiacetic acid, n-hexadecyl iminodiacetic acid, n-octadecyl iminodiacetic acid, n-licosyl iminodiacetic acid, n-triacontyl iminodiacetic acid and the like.

While the reaction products of the 1,2-disubstituted imidazolines and the iminodiacetic acids of the classes herein described are all effective rust inhibitors, it is not to be implied that all are equivalents since the specific activity of the various products may vary to some extent, depending upon the nature and severity of the service, the nature of the metal surfaces, the relative solubility of the products in the media in which they may be used, etc. For example, products prepared with the n-alkyl substituted iminodiacetic acids exhibit somewhat better properties in water tolerance tests, i.e., exhibit less water solubility and less tendency to cause haze, than do some of the products prepared with the corresponding n-acyl substituted iminodiacetic acids.

The inhibitors of the present invention are effective in normally oleaginous materials, especially petroleum oils, particularly normally liquid hydrocarbon oil fractions, such as light mineral fractions, for example, mineral oil distillates in the gasoline distillation range, naphthas, kerosene, fuel oils, burner oils, and the like. As noted above, the inhibitor herein described can be used in concentrations of from about 0.0005% to about 0.01%, by weight. For most product, adequate anti-rust protection is attained by using 0.1 to 3.0 pounds of the active inhibitor per 1,000 barrels of the light oil product. The inhibitor can be formed in situ in the oil by the addition of the imidazoline and iminodiacetic acid in the proper proportion. However, it is more desirable to prepare the inhibitor and then add the desired amount to the light oil product. The inhibitor then can be prepared under controlled conditions in any quantity, and, advantageously can be produced and handled in the form of a concentrate solution. Thus the inhibitors can be prepared in liquid concentrates comprising from about 10% to about 60%, by weight, solutions of the inhibitor in a hydrocarbon solvent such as kerosene, naphtha, toluene, xylene, a mixture of n-butyl alcohol and xylene or a solution of isopropyl alcohol in water as above disclosed.

While in many applications of the present invention the herein described corrosion inhibitor will be added to a finished product, there are special situations where the inhibitor will be added to the product, e.g. petroleum, undergoing processing in order to prevent or inhibit corrosion to the parts of the processing equipment which come in contact with the material containing corrosive compounds. For example, the inhibitor can be injected into a stream of petroleum being processed in order to inhibit corrosion to metal surfaces of such equipment subjected to contact with the petroleum fractions containing corrosive material.

The preparation and evaluation of representative inhibitors of this invention will be illustrated by the following examples and tests.

EXAMPLE I

5.6 grams (0.016 mol) 1-hydroxyethyl, 2-heptadecenyl imidazoline and 5.0 grams (0.016 mol) n-lauroyl inminodiacetic acid were mixed in 15.9 grams of a solvent mixture of 30% n-butyl alcohol and 70% xylene and the mixture heated to 150° F. with stirring until the solution was clear, and then cooled to room temperature (about 70–75° F.). A clear red liquid was obtained. The finished product contained 40% (wt.) inhibitor and 60% (wt.) solvent mixture.

EXAMPLE II

In this example the product was prepared as in Example I, except that the reaction was carried out in sufficient kerosene to give a finished product of 50% (wt.) inhibitor and 50% (wt.) kerosene.

EXAMPLE III

This product was prepared as in Example I, except that the reaction was carried out in sufficient xylene to give a finished product containing 50% (wt.) of the reaction product.

EXAMPLE IV

Same as Example I, except that the reaction was carried out in a solvent mixture of 40% (wt.) n-butyl alcohol and 60% (wt.) kerosene. Sufficient solvent was used so that the final composition consisted of 50% (wt.) of the reaction product and 50% (wt.) of said solvent mixture.

EXAMPLE V

A mixture of 4.9 grams (0.014 mol) 1-hydroxyethyl, 2-heptadecenyl imidazoline and 5.0 grams (0.014 mol) n-hexadecyl iminodiacetic acid and 15.0 grams of a solvent mixture consisting of 30% (wt.) n-butyl alcohol and 70% (wt.) xylene were heated to 140° F. until a clear solution was obtained, and then cooled to room temperature (70–70° F.). The recovered product was a stable clear orange-colored solution. The finished product contained 40% (wt.) inhibitor and 60% (wt.) solvent mixture.

EXAMPLE VI

A mixture of 4.6 grams (0.013 mol) 1-hydroxyethyl, 2-heptadecenyl imidazoline and 5.0 grams (0.013 mol) n-octadecyl iminodiacetic acid and 14.4 grams of a solvent consisting of 30% (wt.) n-butyl alcohol and 70% (wt.) xylene were heated to 140° F. until a clear solution was obtained, and then cooled to room temperature (70–75° F.). The recovered product was a stable clear orange-colored solution; the finished product containing 40% (wt.) inhibitor and 60% (wt.) solvent mixture.

EXAMPLE VII

A mixture of n-lauroyliminodiacetic acid and 1-(2-hydroxyethyl)-2-heptadecenyl imidazoline in a 1:1 molar ratio in a solvent consisting of 75% (wt.) isopropyl alcohol in water was stirred at room temperature until a clear solution was obtained. The reaction product was recovered as a clear red solution containing 40% active ingredient in a solvent consisting of 75% isopropyl alcohol in water.

EXAMPLE VIII

A mixture of lauryliminodiacetic acid and 1-(2-hydroxyethyl)2-heptadecenyl imidazoline in a 1:1 molar ratio in a solvent consisting of 75% (wt.) isopropyl alcohol in water was stirred at room temperature (70–75° F.) until a clear solution was obtained. The reaction product was recovered as a clear red solution containing 40% active ingredient in a solvent consisting of 75% isopropyl alcohol in water.

The rust inhibiting properties of the above compositions and related compositions of this invention, were evaluated by the following tests:

Navy static drop test

In this test, which is a widely used static rusting test, shallow depressions or dimples are punched in the centers of triangular steel specimens, which are placed in small beakers and covered with gasoline containing the rust inhibitor. After allowing time for the inhibitor to adsorb on the steel surface, a drop of deionized water is placed in the dimple or depression below the surface of the gasoline. The beakers are held in a water bath at 100° F. and the specimens observed visually for 24 hours for rust-

ing of the steel beneath the water drop. The amount of rust under the water drop after this time is rated as: none, light, medium, heavy, or, extra heavy.

This test is described by Baker et al. in "Polar-Type Rust Inhibitor," in Industrial and Engineering Chemistry, vol. 41, No. 1, p. 137 (1949).

Modified Navy static drop test

The above Navy static drop test is modified to approximate so-called "intermittent" conditions in which steel surfaces are exposed alternately to inhibited gasoline and condensed water. In this test the triangular specimens, prepared as in the Navy static drop test, are soaked in inhibited gasoline. They are then removed from the gasoline, drained, and placed in clean beakers containing a little water on the bottom to maintain a humid atmosphere. A drop of water is then placed in each dimple, the beakers covered, and the test specimen observed for rusting under the water drop for a 24-hour period. The specimens are rated as described in the standard Navy test.

Bottle test

This test is carried out as follows:

A sheet of .005 in. mild steel stock is abraded with #2 followed by #00 emery cloth and then with steel wool. Coupons 6" x ½" are cut from this sheet, wiped with a dry cloth, and immersed in 1 pint wide mouth bottles containing the test mixtures. These mixtures consist of 250 ml. of oil plus inhibitor solutions, and 100 ml. of boiled distilled water. The bottles are covered with a Teflon sheet and a screw cap, rolled ten times horizontally to mix the contents, and allowed to stand upright for 5 days. Thus, portions of the specimen are exposed to the aqueous, oil, and vapor phases. The amount of rust which appeared on the steel in each phase is rated as none, light, medium, heavy, or extra heavy, as in the Navy test. Readings were taken daily, and the final results are recorded after five days.

Indiana Conductometric Test (Dynamic)

This test, which quantitatively measures corrosion rates, depends upon the measurement of the change in electrical resistance of a steel test strip immersed in the corrosive medium. The change in resistance is simply related to the decrease in the thickness of the test specimen caused by corrosion. In the test, specimen holders are designed to make electrical connections to two steel strips suspended in large glass test tubes. A mixture of gasoline containing the rust inhibitor plus 1% deionized water is placed in the tube and the mixture stirred rapidly for 24 hours at 100° F. From the observed change in electrical resistance of each test specimen during the course of the test, quantitative corrosion rates are calculated in terms of inches penetration per year.

Indiana Conductometric Test (Static)

The above test is modified for testing under static conditions. In the modified method approximately equal volumes of deionized water and the inhibited gasoline are placed in the test tubes and the mixture stirred briefly to allow the inhibitor to be distributed between the two phases. Stirring is then discontinued and the test specimens are placed in the gasoline phase to reach adsorption equilibrium, after which they are lowered into the aqueous phase where resistance changes are observed as a measure of rusting during the 24-hour period.

Modified Indiana Conductometric Test (Dynamic)

This test is similar to the above described Indiana Conductometric Test (Dynamic) except that ten percent stock solutions of ammonium chloride are prepared in deionized water and adjusted to pH levels of 2 and 6 with hydrochloric acid and ammonium hydroxide. 1.75 ccs. of this stock solution of the desired pH level is placed in the bottom of the large glass test tubes and 175 ccs. of a sour virgin light naphtha added. The steel test specimens are placed in the test tube and the mixture stirred rapidly for seven hours at a temperature of about 100° F. When the test is conducted in an atmosphere other than air, the appropriate gas or gas mixture, for example 1% H_2S in hydrogen, is introduced into the test tube, either into the vapor space above the liquid or bubbled through the liquid. As in the Indiana Conductometric Test, from the observed change in electrical resistance of each test specimen during the course of the test, quantitative corrosion rates are calculated in terms of inches penetration per year.

Typical data obtained by subjecting the products of the present invention to the above tests are tabulated in the following tables, and demonstrate the effectiveness of the herein described products in inhibiting rusting in light oils products.

TABLE I.—NAVY STATIC DROP TEST

[Rust ratings for 4 specimens in 24 hours]

Inhibitor	Concentration, lbs./1,000 bbls.	Gasoline	Kerosene	Heater oil	Furnace oil
Blank		XXXX[a]	XXXX.	XXXX.	XXXX.
Product Example I	2	LLLL.	NHHH.	LLLL.	
Do	5	NNNL.	LLLL.	NNLL.	
Product Example II	2	LLLL.			
Do	5	NNNL.			
Product Example IV	2	LLLL.			
Do	5	NLLL.			
Product Example V	2	NNNN.			
Do	5	NNNN.			NNNN.
Product Example VI	2	NNNL.			
Do	5	NNNN.			NNNN.

[a]Heavy rust in 8 hours.

Legend:
N=no rust.
L=light rust.
M=medium rust.
H=heavy rust.
X=extra heavy rust.

In the modified Navy Test after 24 hours uninhibited gasoline had a rust rating of "heavy," while the gasolines inhibited with 2 and 5 pounds per 1000 barrels of the product of Example I were rated "light."

The "Bottle Test" ratings of the inhibitor of Example I in various light oil products are tabulated in Table II.

TABLE II.—BOTTLE TEST RATINGS IN LIGHT OILS PRODUCTS

Inhibitor	Ratings in Aqueous Phase				Ratings in Oil Phase			
	A	B	C	D	A	B	C	D
Control (no inhibitor)	X	X	X	X	H	H	L	M.
2 pounds of the product of Example I per 1,000 barrels	L	X	L	X	N	N	N	L.
5 pounds of the product of Example I per 1,000 barrels	N	N	L	M	N	N	N	L.

Legend:
A=Gasoline.
B=Kerosene.
C=Heater oil.
D=Diesel fuel.
N=No rust.
L=Light rust.
M=Medium rust.
H=Heavy rust.
X=Extra heavy rust.

Data obtained in the Conductometric Test, both static and dynamic, are given in Table III. The data were obtained on uninhibited gasoline and gasoline containing the product of Example I in concentrations of 2 and 5 pounds per 1000 barrels. For each concentration the table shows the number of experiments and the geometric mean of the corrosion rates.

TABLE III.—CONDUCTOMETRIC TEST

[Static test]

Inhibitor	Concentration, lbs./1,000 bbls.	No. of tests	Corrosion rate, geometric mean, mils/year
Blank		11	10.76
Product of Example I	2	4	0.17
Product of Example II	2	7	0.29
Do	5	9	0.22
Product of Example IV	2	1	0.25
Product of Example V	2	1	0.12
Product of Example VI	2	2	0.13

[Dynamic test]

Blank		6	6.74
Product of Example II	2	4	0.15
Do	5	4	0.14
Product of Example V	2	1	0.21
Do	5	2	0.21
Product of Example VI	2	2	1.30
Do	5	2	0.66

The corrosion-inhibiting effect of the additives of the present invention in the presence of corrosive refinery stocks is demonstrated by the data in Table IV. These data were obtained by the Modified Indiana Conductometric Test (dynamic) described above using as the corrosive medium a sour pipe still virgin light naphtha mixed with an aqueous phase consisting of 10% ammonium chloride in tap water. The pH value of the test media was adjusted with ammonia and hydrochloric acid. These are very severe test conditions, comparable to highly corrosive low pH conditions encountered in petroleum refinery processing.

TABLE IV.—CORROSION RATES—INCHES PER YEAR—CONDITIONS: RAPID STIRRING—AIR PRESENT

Concentration (p.p.m.)	pH=2			pH=6		
	Product Ex. VII	Product Ex. VIII	Product A[1]	Product Ex. VII	Product Ex. VIII	Product A
Blank	0.221	0.221	0.221	0.171	0.171	0.171
1	0.285	0.351	----------	0.0294	0.0456	0.207
2	0.0310	0.186	----------	0.0029	0.0040	0.221
5	0.0052	0.0159	0.194	0.0009	0.0018	0.232
10	0.0009	0.0014	0.170	0.0002	0.0013	0.167
20	0.0005	0.0007	0.0769	0.0005	0.0010	0.121
40	0.0008	0.0909	0.0584	0.0004	0.0005	0.0169
80	0.0006	0.0007	0.0580	0.0005	0.0004	0.0033

[1] Product A is a commercial refinery corrosion inhibitor.

Data, similar to those given in Table IV but obtained in an atmosphere of 1% H_2S in a hydrogen atmosphere, are given in Table V below. In other respects, the test conditions were the same as the test used in respect to the data obtained in Table IV.

TABLE V.—CORROSION RATES—INCHES PER YEAR—CONDITIONS: RAPID STIRRING—1% H_2S IN H_2 ATMOSPHERE

Concentration (p.p.m.)	pH=2			pH=6	
	Product Ex. VII	Product Ex. VIII	Produst A[1]	Product Ex. VII	Product A
Blank	0.242	0.242	0.242	0.157	0.157
1	0.0521	0.0743	0.167	0.154	----------
2	0.0462	0.0760	0.135	0.0104	0.287
5	0.0425	0.0635	0.0488	0.0024	0.141
10	0.0012	0.0032	0.0787	0.0035	0.0189
20	0.0018	0.0043	0.0218	0.0035	0.0048
40	0.0020	0.0065	0.0231	0.0059	0.0040
80	0.0009	0.0007	0.0007	0.0036	0.0039

[1] Product A is a commercial refinery corrosion inhibitor.

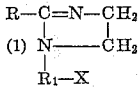
The values given in Tables IV and V are averages of at least 10 determinations, the average deviation being about 3%. The values underlined in Tables IV and V indicate the lowest concentration at which the respective inhibitor brought the corrosion rate below 0.01 inches per year. The above data establish the corrosion inhibiting effectiveness of the inhibitors of the present invention, and demonstrate the adaptability of such compounds as inhibitors for preventing the corrosion and/or rusting of refinery equipment wherein metal surfaces are in contact with oil and water, hydrogen sulfide, air, etc.

Finished light oil products with the inhibitor of this invention can contain other additives known to impart other desired properties, for example, anti-knock agents, anti-oxidants, gum fluxes, sludge dispersants, etc.

Percentages given herein and in the appended claims are weight percentages unless otherwise specified.

I claim:

1. The reaction product obtained by reacting at a temperature of from about 70° F. to about 200° F., 1:1 molar proportions of (a) 1,2-disubstituted imidazoline having the formula



in which R represents unsubstituted aliphatic hydrocarbon of about 8 to about 20 carbon atoms selected from the group consisting of alkane hydrocarbon and alkene hydrocarbon, R_1 is selected from the group consisting of hydrogen and the group—CH_2CH_2—, and X is a polar group selected from the class consisting of hydroxy and amino when R_1 is —CH_2CH_2—, and (b) substituted alkylene iminodiacetic acid having the formula

$$RN[(CH_2)_xCOOH]_2$$

in which R is selected from the group consisting of (a) the acyl radical R'CO—in which R' represents unsubstituted alkane hydrocarbon of about 8 to about 30 carbon atoms and (b) unsubstituted n-alkyl hydrocarbon of about 8 to about 30 carbon atoms, and x is the integer of from about 1 to 3 inclusive.

2. The reaction product as described in claim 1 in which the imidazoline is 1-hydroxy, 2 heptadecenyl imidazoline and the iminodiacetic acid is n-octadecyl iminodiacetic acid.

3. The reaction product as described in claim 1 in which the imidazoline is 1-hydroxyethyl, 2 heptadecenyl imidazoline and the imino-diacetic acid is n-lauroyl iminodiacetic acid.

4. The reaction product as described in claim 1 in which the imidazoline is 1-hydroxy-ethyl, 2 heptadecenyl imidazoline and the iminodiacetic acid is n-hexadecyl imino-acetic acid.

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