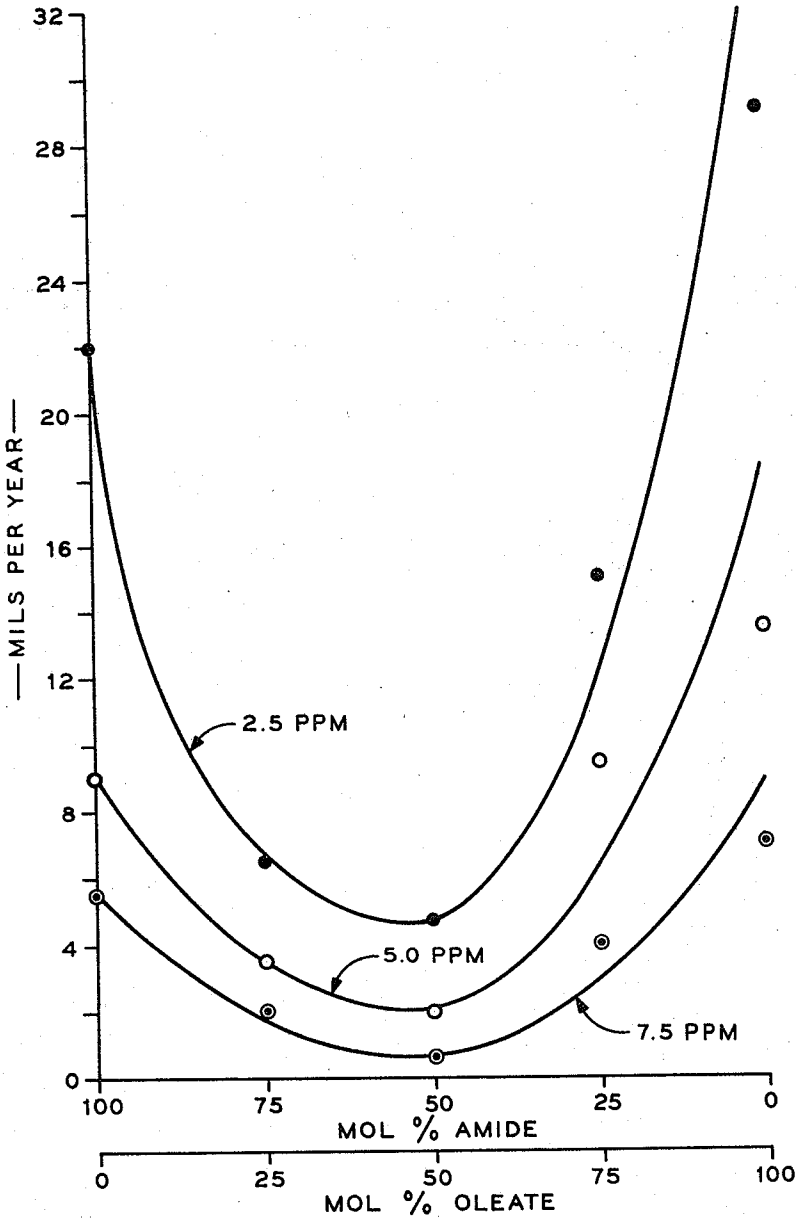
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REFINERY CORROSION INHIBITOR

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CORROSION INHIBITION



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REFINERY CORROSION INHIBITOR

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The present invention concerns corrosion-inhibiting compositions for use in petroleum refining operations, in particular, compositions which are effective in reducing corrosion occurring in overhead systems of refinery treating equipment, and specifically in fractionation columns, in the course of processing different crude oil feedstocks. The metal equipment in the upper portions of these columns or towers is particularly vulnerable, and the rates of corrosion as high as 100 mils a year (and often higher) are observed. Both steel and copper-containing alloys, e.g., the so-called "Admiralty Metal," are similarly affected, and heat exchangers and condensers equipped with Admiralty brass bundles, when used to cool, collect and recover (or recycle) hot hydrocarbon fractions which pass overhead in refinery distillation units, are subject to early deterioration and failure.

Various remedies for preventing and/or reducing corrosion of refinery equipment, which is either due to acid components in the hydrocarbon feeds or to oxygen admixed in the water present in the fractionation system, have been proposed in the past.

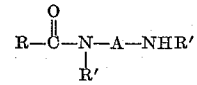
The usual procedure to combat corrosion is to introduce or inject oxidation and/or corrosion inhibitors in counterflow to the vapors rising overhead in the system. These "rundown" inhibitors form a film on the internal metal surfaces of the refinery treating equipment, particularly in the upper portions of the fractionating columns in heat exchangers and condensers.

A number of such likely inhibitors have been mentioned in the prior art, in particular, materials containing aminonitrogen atoms such as high molecular weight monoamines and polyamines, acylated polyamines, imidazolines, amides, carboxylate salts of high molecular weight amines and polyamines, etc.

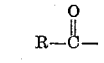
However, while on the basis of these prior art disclosures, one would generally expect some anti-corrosive action from aminonitrogen-containing materials, in most cases it is well nigh impossible to predict that a particular inhibitor may or may not be successfully utilized in the refinery for preventing corrosion, and particularly for preventing corrosion in the upper portions of fractionating columns and in overhead systems which comprise condensers and other metal equipment. The inhibiting action does not maintain a steady rate in the case of each particular inhibitor, but is more apt to be sporadic and variable. Furthermore, the use of some such inhibitors, even though in very low concentrations, is often found to affect adversely the quality of the ultimately recovered, finished product, such as gasoline. In particular, if the inhibitor is prepared from raw materials containing polyunsaturated acids, the finished petroleum product, such as gasoline, frequently becomes degraded and is prone to cause difficulties, such as engine-deposit formation. In another instance, certain amine carboxylates which could be used as effective corrosion inhibitors are not sufficiently soluble in the hydrocarbon fuel into which they are injected and thus present a deposit problem when they are contained in the finished gasoline.

I have now found that the aforementioned corrosion of the refinery equipment can be effectively reduced, if not completely prevented, by employing to inhibit it a composition comprising, as its essential ingredient, a mixture of a particular aminoamide and a certain kind of salt of this aminoamide in an effective molar ratio to

each other. The aminoamide component of this inhibitor mixture is an aminoamide of a straight-chain C_{16}–C_{22} fatty acid (saturated or unsaturated), such as are derived from naturally-occurring fats and oils. This aminoamide may be represented by the general formula:



in which



is the acyl residue of a C_{16}–C_{22} straight-chain fatty acid, A is an alkylene radical of 2 to 4 carbon atoms, and, in the two occurrences of R′, one is hydrogen and the other is selected from the group consisting of aminoethyl and hydroxyethyl radicals. The salt component of the inhibitor mixture is a particular kind of carboxylate, namely, a salt of C_{16}–C_{22} straight-chain fatty acid, of the aforedescribed aminoamide. The effective mol ratio of the aminoamide to the carboxylate in the mixture ranges from about 4:1 to about 1:4, and preferably from about 1:3 to about 3:1.

The combinations of oleic acid aminoamides (oleamides) and their corresponding oleate salts in the ratios given hereinabove are particularly preferred, because of the easier solubility of the oleates in hydrocarbon liquids. However, combinations of other aminoamides and their corresponding carboxylates, as defined hereinbefore, can be effectively introduced into the hydrocarbon feedstocks being processed at the refinery to combat corrosion of the metal equipment, using these combinations in the form of concentrates, that is, dissolved in suitable organic solvents, such as compatible hydrocarbons and/or alcohols.

By introducing the corrosion-inhibiting composition comprising a mixture of the aminooleamide and its oleic acid salt in the aforementioned ranges of mol ratios, and in an amount which, although small, is sufficient to inhibit effectively the corrosion into the refinery treating equipment, specifically in the upper portions of the fractionation columns, piping for overhead effluent, coolers, condensers and reboilers for recycling (refluxing) the condensate, it becomes possible to suppress, or at least to reduce drastically, the otherwise unavoidable corrosion. A definite co-action (synergism) is apparently exerted by the two active components of the inhibitor—the oleamide and its oleate—permitting to control and to minimize the corrosion to the extent which could not be expected from perusing the disclosures of the prior art. In fact, corrosion is reduced several fold (from four to ten times), as compared with the use of the amide or its salt alone in the same amounts of from about 1 to about 25 p.p.m. (parts per million of the hydrocarbon feedstock being processed), and preferably from about 2 to about 20 p.p.m., when fed into the fractionation system at the same feed rates.

The corrosion-inhibiting compositions of the present invention, while being soluble in the hydrocarbon fuel feedstocks treated at the refinery and being sufficiently stable to withstand the temperatures in the fractionation systems, are at the same time sufficiently volatile to be carried along with the overhead vapors from the top of these columns into the condensers, thereby providing protection against the corrosion of this latter equipment as well.

The introduction of the corrosion inhibitors of this invention into the refinery equipment presents substantially no difficulties and may be effected at any convenient point of an overhead system. They are fed in through the appropriate inlet piping at the top or dome of a distillation column, such as a reflux vapor line and/or reflux return line, dissolved, for instance, in a suitable hydrocarbon solvent, preferably boiling from about 150 to

about 400° F., e.g., kerosene, and in concentrations from about 10 to about 60%, preferably from about 25 to about 30%.

The feed rates of the inhibitor may vary, depending on reflux ratios and the capacity of the particular equipment, as well as on the corrosiveness of the feedstock being treated, the pH of the given system, and the susceptibility of the particular metal equipment to corrosion, especially in overhead systems. For instance, in the case of conventional refinery reflux ratios of the order of 4:1, the inhibitor solution of 25% in kerosene can be effectively employed to control corrosion at feed rates from about 0.03 gal./hr. to about 0.15 gal./hr. for a throughput of about 800 barrels/hr., that is so as to provide approximately 1 to 5 p.p.m. total inhibitor concentration in the overhead flow. Higher inhibitor concentrations may be used, if necessary.

The inhibitor composition is prepared in any suitable conventional manner, for instance, as described in U.S. Patent No. 2,839,372 of Lindstrom and Barusch, or by reacting oleic acid with hydroxyethyl-substituted ethylenediamine (or with a diethylenetriamine) at about 380–390° F., so as to remove two mols of water; thereupon hydrolyzing (one mol of water) at 110–120° F.; and then forming an oleate of the resulting aminooleamide in a known manner to obtain a mixture of the aminoamide and its oleate in a mol ratio from about 4:1 to about 1:4, and preferably from about 3:1 to about 1:3.

The unexpected, enhanced anticorrosive action of the inhibiting composition of the present invention was observed and confirmed in a large number of laboratory tests as well as in actual refinery operations.

In the laboratory, corrosion was determined by means of an apparatus known in the trade under the name of "Corrosometer." Essentially its consists of a metal strip or probe, the electrical conductivity of which can be balanced in an electrical (Wheatstone) bridge against that of a similar strip of the same metal, but embedded in (coated with) a plastic material so as to be impervious to the corrosive liquid.

A glass vessel or flask, provided with a stirrer, a reflux condenser, and a thermometer, was used for the tests. This flask received 400 ml. of a base fuel made up of 75% by volume of isooctane and 25% by volume of toluene. Because, on its being corroded, the unprotected probe increases in electrical resistivity, it is possible to obtain the measure of corrosion by balancing on the bridge. First, a null point is obtained by balancing the unprotected test probe against the protected one. After the test probe is exposed to corrosion by a corrosive hydrocarbon liquid, the bridge is balanced again, and the difference in the two conductivity values provides the desired measure of corrosion.

The temperature of the base hydrocarbon fuel in the flask was raised to 100° F., and the stirrer started. The probe was then placed in the fuel containing the corrosion inhibitor for one-half hour to allow formation of a protective film on the mild steel surface thereof. The stirrer was then stopped, and 4 ml. of a 1% solution of ammonium chloride was added. Thereupon a gas stream of hydrogen sulfide and air in a 1:1 volume ratio was bubbled through the fuel, while the temperature was maintained at 100° F., and the stirrer started again. Each hour after the actual start-up of the test, the conductivity of the probe was determined on the bridge, and the values noted were plotted against time to give the measure of corrosion. Testing was continued until a steady rate developed. The base fuel without any inhibitor had an average corrosion rate of about 175 mils per year, and was relatively constant, varying from about 160 to about 180 mils per year, presumably owing to slight differences in temperature and to somewhat different responses of each particular probe. This rate was more severe than the rate actually observed in the fracationation columns at the refinery (which was about 100 mils per year).

A large number of tests of the fuel inhibited with different amounts of the corrosion inhibitor in accordance with the invention were run. The runs lasted as long as twenty hours. Both oleic acid aminoamide of hydroxyethyl ethylenediamine and oleic acid aminoamide of diethylenetriamine in combination with their respective oleate salts were successfully tested as corrosion-inhibiting mixtures. Where no change in conductivity would be noted after this time, the corrosion was considered to be nil. At the termination of these laboratory tests, the ratio of the corrosion rate of inhibited fuel to that of the uninhibited base fuel was determined and converted to percent, and it provided the measure of corrosion reduction.

The significance of the mol ratio of the aminoamide to that of its salt in securing the substantial suppression of corrosion in accordance with the invention is readily perceived from the plot shown in the attached drawing. In this drawing the corrosion in mils per year for three inhibited fuels is plotted against the relative content (in mol percent) of the aminooleamide and the oleate salt thereof in the inhibitor mixture, which was supplied so as to provide 2.5, 5.0 and 7.5 p.p.m. concentrations in the fuel (p.p.m. means parts per one million parts of the base fuel). The spectacular improvement in the region which corresponds to from about 4:1 to about 1:4, and particularly from about 3:1 to about 1:3, ratios of the amide to its oleate salt is clearly apparent.

The effectiveness of the corrosion-inhibiting composition of the invention was also demonstrated in actual refinery operation by tests of several months' duration. In these tests, a battery of several distillation units, which processed crude oil to recover overhead straight-run gasoline fractions in atmospheric columns at 4:1 reflux ratio, was first operated for one month, adding from the top of each column the aminooleamide of hydroxyethyl ethylenediamine at the rate of about 0.28 gal./hr. so as to provide a fairly high inhibitor concentration of 10 p.p.m. in the crude-treating battery. The pH of the water in the overhead system was controlled at 5.5 to 6.5. The corrosion rate measured with the aid of both steel and Admiralty alloy probes, by the same method as in the laboratory tests described hereinabove, was found to amount to from 1 to 4 mils per year. For the next fifteen days of the battery's operation, the amide inhibitor was supplied at the rate of 0.038 gal./hr., providing a concentration of 1.3 p.p.m. in the system. The rate of corrosion went gradually up, showing that the corrosion could be no longer inhibited with this low concentration of the aminoamide. Then this amide inhibitor was replaced by an inhibitor formulated in accordance with the invention, i.e., was made of both the amide and the oleate, though in a mol ratio of 1:1. It was added so as to provide a 1.3 p.p.m. concentration in the hydrocarbon liquid in the overhead system. The corrosion rate in the lower and upper parts of the reflux vapor line reached the level of 1 to 4 mils per year. When the inhibitor composition was again replaced by a mixture made up of one mol of the aminoamide and one-quarter mol of its oleate for ten days, using the same feed rate and providing the same concentration in the hydrocarbon (1.3 p.p.m.), the corrosion rate of 1 to 4 mils per year was maintained. On changing the inhibitor mixture to one containing 0.75 mol of oleate per one mole of the amide, the corrosion rate increased to from 4 to 7 mils per year.

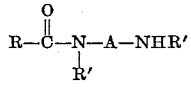
However, when the aminoamide/oleate inhibitor was again substituted a week later by the aminoamide alone, fed at the same rate and providing the same concentration of the aminoamide in the hydrocarbon, the corrosion rate increased at first to 4 to 7 mils per year and, after about two months, to as much as 11 to 14 mils per year. Increasing the concentration of the amide to 11 p.p.m. from the previous 1.3 p.p.m. brought the rate down to 7 to 11 mils per year. Dropping the concentration again to 1.3 p.p.m. resulted in a substantial jump of the rate to 21 to 26 mils a year.

The aforegiven illustrations of the unexpected effect of the corrosion-inhibiting compositions of the invention unquestionably demonstrate their superiority over the previously disclosed materials as possible remedies of refinery equipment corrosion, particularly as regards to overhead systems of fracationation towers.

In conclusion, it is to be understood that the invention as set forth hereinabove may be modified in many ways without departing from the scope thereof, provided they fall within the definitions of the following claims.

I claim:

1. A composition for inhibiting corrosion occurring in petroleum refinery fractionation equipment, said composition comprising a mixture of (1) an aminooleamide of the general formula:



in which



is the acyl residue of oleic acid, A is an alkylene radical

of 2 to 4 carbon atoms, and, in the two occurrences of R', one is hydrogen and the other is selected from the group consisting of aminoethyl and hydroxyethyl radicals, and (2) an oleate salt of said aminooleamide, the mol ratio of said amide to said oleate being in the range from about 4:1 to about 1:4.

2. A composition as defined in claim **1** wherein said mol ratio of the aminoamide to the oleate is in the range from about 3:1 to about 1:3.

3. A composition as defined in claim **1** wherein the aminooleamide component is oleic acid amide of hydroxyethyl ethylenediamine.

4. A composition as defined in claim **1** wherein the aminooleamide component is oleic acid amide of diethylenetriamine.

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