United States Patent [19]

Kray

[11] **3,909,215**

[45] **Sept. 30, 1975**

[54] **RUST INHIBITORS FOR HYDROCARBON FUELS**

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[22] Filed: **Mar. 27, 1973**

[21] Appl. No.: **345,402**

[52] **U.S. Cl.** **44/62;** 44/63; 252/405

[51] **Int. Cl.**[2] **C10L 1/14**

[58] **Field of Search** 44/62, 63; 252/405

[56] **References Cited**

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[57] **ABSTRACT**

A novel rust inhibitor mixture for use in hydrocarbon fuels comprising an α-olefin-maleimide copolymer and a hydrocarbyl amine, amide or imidazoline is disclosed. A method of inhibiting rust in fuel oils is also disclosed.

13 Claims, No Drawings

RUST INHIBITORS FOR HYDROCARBON FUELS

DESCRIPTION OF THE INVENTION

This invention relates to a rust inhibitor composition and more particularly to an improved rust inhibiting composition for use in petroleum oils.

In the handling of hydrocarbon fuel oils, especially heating and furnace oils, it is frequently necessary to store the liquids for a considerable period. In the colder northern regions of the United States, home owners often store several months supply of heating or furnace oil in iron tanks. Small amounts of water inevitably derive access to the tank and form a thin film or water layer at the bottom of the tank. In the coastal regions, a great number of these tanks also tend to collect salt water thereby compounding the problems.

As a result of the presence of water in the metal vessels, rusting or corrosion of the areas contacted by the water occurs. The rust formation is caused by both long cell and local cell corrosion with long cell corrosion being accentuated in the salt water environment. If the rusting processes are not checked, the tank will eventually develop weak or thin spots with ensuing leakage.

The formation of rust can be suppressed by adding a conventional water-soluble rust inhibitor to the system. Typical of these rust inhibitors include dichromate solutions, sodium nitrite pellets, water soluble amines, etc.

These conventional inhibitors are effective in suppressing rust formation in the tank, but are burdened by several ancillary problems caused in part by the inhibitor in the application procedure. For examples, the inhibitors must be added to each tank by the tank owner. In the case of residential heating oil tanks, the home owner is often responsible for its addition which is often overlooked or forgotten. Another problem is that many of the additives cause in-line nozzles to become plugged. Typical nozzles which are often effected are those employed in residential heating oil furnaces. Another problem is the adverse effect of these conventional inhibitors on the stability of the hydrocarbon fuel or other additives present therein, thereby causing precipitates to form within the liquid solution. In many instances, these precipitates are sufficient to cause blockage of in-line filters.

It is therefore an object of this invention to provide an improved rust inhibitor.

It is another object of this invention to provide an improved rust inhibitor for hydrocarbon fuels which does not cause precipitates within the fuel.

It is another object of this invention to provide a hydrocarbon fuel containing an improved rust inhibitor.

It is an additional object of this invention to provide a method for inhibiting rust.

Other and related objects of this invention will become apparent from the following description thereof and accompanying claims.

SUMMARY OF THE INVENTION

The aforementioned objects and their attendant advantages are realized by adding to an oleophilic organic liquid a small amount of a mixture comprising (1) a copolymer of an alpha-olefin having from 8 to 30 carbons and an N-substituted maleimide wherein the N-substituents on the maleimides are organic radicals free of aromatic groups and having from 3 to 60 carbon atoms and from 1 to 5 amine nitrogens, and where the copolymer has from 4 to 20 repeating olefin-maleimide units, and (2) a hydrocarbyl amine, amide, imidazoline or mixtures thereof having from 3 to 60 carbons and from 1 to 10 nitrogen atoms with a carbon to nitrogen atomic ratio from 5 to 30:1. The ratio of the copolymer to the hydrocarbyl amine, amide or imidazoline generally varies within the range of 10 to 0.75 parts of copolymer per part of hydrocarbyl amine.

The above-defined rust inhibitor mixture is soluble within the oleophilic organic liquid and does not cause the organic liquid to become unstable or form precipitates. Also, the inhibitor mixture may be blended with the organic liquid prior to being transported and stored. In this embodiment a rust inhibitor does not have to be extraneously added to the organic liquid in each tank. The inhibitor mixture also does not induce nozzle plugging problems, and accordingly, may be successfully employed in heating oils without plugging the furnace jets.

Although the exact mechanism of the two components of the inhibitor mixture in effecting rust inhibition is not known, it is known that the components combine in a synergistic manner to effect superior rust inhibition over either component individually and over no additive.

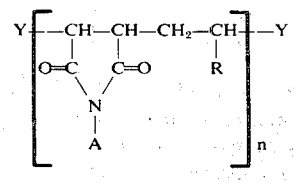
DETAILED DESCRIPTION OF THE INVENTION

In accordance with the practice of this invention, improved rust inhibition can be realized with an oleophilic organic liquid by admixing with the liquid from 0.005 to 1 weight percent of an olefin-maleimide copolymer, more particularly defined hereinafter, and from 0.01 to 0.02 weight percent of a hydrocarbyl amine, amide, or imidazoline also defined hereinafter.

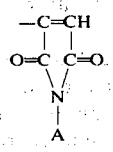
α-OLEFIN-MALEIMIDE COPOLYMER

The α-olefin-maleimide copolymers which may be employed in the practice of this invention are oil soluble alternating copolymers of N-substituted maleimides and aliphatic α-olefins of from 8 to 30 carbons. The copolymers have an average of 4 to 20 maleimide groups per molecule. That is, a succinimide group alternates with an alkyl substituted ethylene. The substituents on the nitrogen of the maleimide may be the same or different and are organic radicals composed essentially of carbon, hydrogen and nitrogen having a total of 3 to 60 carbon atoms and from 1 to 5 amine nitrogen atoms. The substituents on the succinimide nitrogen can be aminoalkyl, polyaminoalkylene or the mono-N- or di-N,N-aliphatic hydrocarbyl substituted derivatives thereof. (By the term "aliphatic hydrocarbyl" is intended organic radicals free of aromatic unsaturation composed solely of carbon and hydrogen.) The total molecular weight of the molecule will generally be in the range of about 2,000 to 15,000, more usually in the range of about 4,000 to 10,000.

The polymers of this invention have the following general structure:

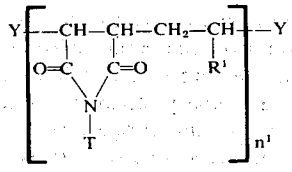


wherein A is an organic radical of 3 to 60 carbon atoms, more usually from 3 to 30 carbon atoms having from 1 to 5 amine nitrogens and free of aromatic unsaturation. The symbol A includes aminoalkyl, polyalkylene amine, N-hydrocarbyl aminoalkyl, N-hydrocarbyl polyalkylene amine and N,N-dihydrocarbyl aminoalkyl, wherein the hydrocarbyl groups are free of aromatic unsaturation. Usually, the hydrocarbyl groups will be aliphatic; that is, acylic, but may be alicyclic or taken together with the nitrogen, heterocyclic. R is a hydrocarbyl, preferably an alkyl, having from 6 to 28 carbon atoms, and n is an integer from 4 to 20. Usually R will be from about 8 to 20 carbon atoms, more usually from 12 to 18, and n from about 4 to 20, and preferably from 6 to 16. The symbol Y represents the terminal end of the chain and may be hydrogen, an olefinic group (—CH=CHR) or



or an hydroxy group.

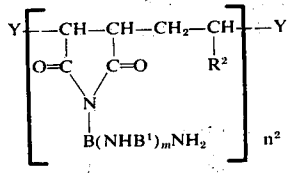
One subgenus within the scope of the invention has the following formula:



wherein T is aminohydrocarbyl free of aromatic unsaturation, generally of 5 to 26 carbon atoms (aminohydrocarbyl free of aromatic unsaturation is a monovalent organic radical composed essentially of carbon, hydrogen and one nitrogen, wherein the nitrogen is present only as primary, secondary or tertiary amines, and the radical is aliphatic, alicyclic or heterocyclic having nitrogen as its only annular heteroatom); R^1 is an alkyl radical of 6 to 28 carbon atoms, preferably of 8 to 20 carbon atoms; n^1 is an integer from 4 to 20, more usually from 6 to 16. Y is defined supra.

The particularly preferred compositions of the aminohydrocarbyl substituted compounds are those wherein the aminohydrocarbyl group is aliphatic of 5 to 26 carbon atoms having one secondary nitrogen atom separated by not more than 6 carbon atoms from the succinimide nitrogen. The nitrogen atom may be part of the chain or may be pendant from the chain.

The polyalkylene amine compositions will have the following formula:



wherein B and B^1 are alkylene of 2 to 6 carbon atoms, more usually from 2 to 3 carbon atoms, m is an integer from 0 to 4, usually from 0 to 3, R^2 is an alkyl radical from 6 to 28 carbon atoms, preferably from 8 to 20 carbon atoms, and n^2 is an integer from 4 to 20, more usually from 6 to 16. Y is defined supra.

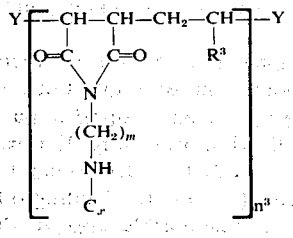
While, usually, the alkylene polyamines will be unsubstituted, if desired, substituted alkylene polyamines may be used having from 1 to 2 aliphatic hydrocarbyl substituents on the nitrogen atoms.

The remaining 2 valences of the polymer may be satisfied in a variety of ways. One or both of the valences may be satisfied by a radical derived from the polymer initiator. The polymeric chain may terminate by transfer, coupling or disproportionation, resulting in end groups of hydrogen, alkyl groups, alkenyl groups, succinimide or maleyl groups or radicals derived from the initiator.

Illustrative of various aminohydrocarbyl radicals are aminohexyl, aminodecyl, aminooctadecyl, N-hexylaminohexyl, N-decylaminopropyl, N-hexadecylaminohexyl, N-hexylpyrrolidinyl, N,N-diethylaminobutyl, N-abietyl 3-aminopropyl, N-dihydroabietyl 2-aminoethyl, etc.

Illustrative of various alkylene amine and polyalkylene polyamine radicals are tetraethylenyl tetramine, triethylenyl triamine, diethylenyl diamine, dipropenyl diamine, tripropenyl triamine, etc.

A particularly preferred group of compounds have repeating units of the formula:



wherein R^3 is an alkyl radical from 8 to 20 carbon atoms, m^1 is an integer from 2 to 3, C_x indicates an aliphatic hydrocarbon radical having x number of carbon atoms wherein x is an integer from 8 to 20, i.e., C_{8-20}, and n^3 is an integer from 6 to 16. The aliphatic radical may be straight chain or branched, free of aliphatic unsaturation or unsaturated, particularly olefinically unsaturated. Y is defined supra.

Illustrative of the particularly preferred substituents on the succinimide nitrogen are N-octyl 3-aminopropyl, N-decyl, 2-aminoethyl, N-dodecyl 2-aminoethyl, N-hexadecenyl 2-aminoethyl, N-octadecenyl 3-aminopropyl, N-tetrapropenyl 2-aminoethyl, N-octadecadienyl 2-aminoethyl, N-hexadecenyl 3-aminopropyl, N-octadecyl 3-aminopropyl, N-octadecenyl 2-aminoethyl, etc.

The compounds of this invention are readily prepared by copolymerizing an aliphatic 1-olefin from 8 to 30 carbon atoms with maleic anhydride by means of free radical catalysis and then combining the resulting polymer with the desired amine at elevated temperatures to form the alternating N-substituted polysuccinimide.

The copolymerization of maleic anhydride with aliphatic 1-olefins is well known in the art. See, for example, U.S. Pat. No. 3,051,562.

The olefins which find use include decene, dodecene, tetradecene, hexadecene, octadecene, eicosene, docosene, tetracosene, hexacosene, octacosene, triacontene, tridecene, pentadecene, heptadecene, nonadecene, tetrapropylene, tetraisobutylene, hexapropylene,

etc. Preferably, a mixture of olefins will be used rather than a single olefin. When using mixed olefins, superior fuel solubility is obtained. The mixture will generally have not more than 50 per cent of any single olefin, and preferably not more than 30 mole per cent of any single olefin.

The free radical catalyst may be any organic compound which at a temperature in the range of 50° to 100°C. decomposes to form free radicals which may then initiate the polymeric chain, although temperatures outside this range may be used advantageously under some conditions. The most popular organic free radical agents are the peroxidic initiators—hydroperoxide, dihydrocarbyl peroxide, and diacyl peroxide—and azo compounds. Illustrative of hydroperoxide catalysts are cumyl hydroperoxide, pinane hydroperoxide, tert.-butyl hydroperoxide, p-methane hydroperoxide, etc. Illustrative of dihydrocarbyl peroxides are dicumyl peroxide, ascaridole, di-tert.-butyl peroxide, etc. Illustrative of diacyl peroxides are benzoyl peroxide, lauroyl peroxide, acetyl peroxide, 2,4-dichlorobenzoyl peroxide, etc.

In carrying out the various polymerizations, inert hydrocarbons or halohydrocarbons may be used to advantage. Illustrative of such solvents are benzene, toluene, chlorobenzene, etc.

Usually, the solvent will be 20 to 80 weight per cent of the total reaction mixture, more usually about 30 to 70 weight per cent.

The mole ratio of α-olefin to maleic anhydride will generally be about 0.9–1.2:1.2–0.9, more usually about 1:1. The ratio of olefin to catalyst will generally be 1:0.005–0.1 mole ratio, more usually 1:0.01–0.1 mole ratio.

As already indicated, the temperatures will depend upon the catalyst. Temperatures in the range of 50° to 100°C. may be used; more usually the temperature will be in the range of about 75° to 95°C. The time for the reaction will depend on the catalyst used, the amount of material, and the other variables. Generally, at least one hour will be required, and usually the reaction will not be carried out for more than a period of 24 hours.

Depending on the amount of the materials, the catalyst may be added in a single addition or in aliquot portions during the course of the reaction, maintaining a relatively constant concentration of free radicals in the reaction mixture.

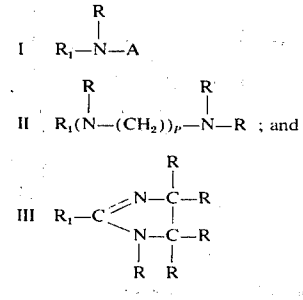
The reaction of the copolymer with the relevant amine is readily carried out by combining the copolymer with the amine in an inert hydrocarbon solvent at elevated temperatures (50°–150°C.) and removing the water as formed. Preferably, an aromatic hydrocarbon solvent is used which allows for azeotroping the water. When the stoichiometric amount of water has been obtained, the reaction is stopped.

HYDROCARBYL AMINE, AMIDE OR IMIDAZOLINE COMPONENT

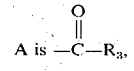
The hydrocarbyl amine, amide or imidazoline which constitutes the second required component of the claimed invention are oil soluble and have a total of 5 to 60 carbons, preferably from 12 to 30 carbons, and from 1 to 10 nitrogens, preferably from 1 to 5 nitrogens, and most preferably from 2 to 4 nitrogens. The atomic ratio of carbon to nitrogen in these compounds may vary between about 5 and 30 carbons per nitrogen, and preferably from 5 to 20:1. Hydrocarbyl amines are preferred and may be primary, secondary, tertiary, or combinations thereof.

The hydrocarbyl portion of the hydrocarbyl amine, amide or imidazoline as employed herein, is a hydrocarbon radical composed essentially of hydrogen and carbon and may be aliphatic, aromatic, alicyclic, or combinations thereof; e.g., aralkyl, alkyl, aryl, cycloalkyl, alkyl cycloalkyl, etc., and may be saturated or ethylenically unsaturated (one or more double bonded carbon pairs, conjugated or non-conjugated).

Exemplary hydrocarbyl amines, amides and imidazolines, as may be employed herein, include those with the following general formulae:



wherein



—R_4OH, R_4NH_2 or hydrogen;

R_1 is a hydrocarbyl having from 8 to 24 carbons, and preferably from 12 to 20 carbons;

R is the same or different univalent radical selected from hydrogen, R_4OH, and R_4NH_2, and preferably hydrogen;

p is an integer from 0 to 4, and preferably from 1 to 3; and

Exemplary compounds falling within the definition of Formula I include octylamine, laurylamine, oleylamine, N-propyloleylamine, N,N-di(ethanol)oleylamine, N-(aminoethyl)-N-(aminopropyl)oleylamine, N-laurylacetamide, N-oleylacetamide, etc.

Compounds falling within the scope of Formula II include N-oleyl ethylene diamine, N-lauryl ethylene diamine, N-octyl trimethylene diamine, N-oleyl-2-aminoethyl ethylene diamine, N-lauryl diethylene triamine, N-oleyl-1,2-propylene diamine, N-oleyl triethylene tetramine, N-oleyl tetraethylene pentamine, N-oleyl-N',N'-dimethylpropylene diamine, N-oleyl-N,N',N'-trimethyl diethylene triamine, etc.

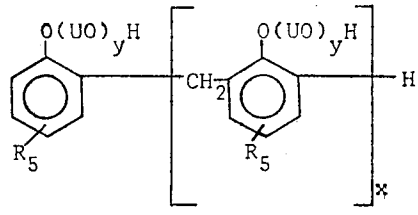
Compounds falling within the scope of Formula III include lauryl ethyl imidazoline, oleyl ethylol imidazoline, etc.

OTHER COMPONENTS

In addition to the afore-mentioned rust inhibitor components, other additives may be incorporated into the oleophilic liquid without adversely affecting the superior rust inhibiting properties. One type of additive is a demulsifier. When the rust inhibitor mixture is combined with the oleophilic, the combined solution becomes more susceptible to emulsify water. Thus, a part of the water present in storage tanks and vessels containing the oleophilic liquid, is emulsified within the

liquid and transported from place to place with the oleophilic liquid. A demulsifier is therefore often advantageously employed to restore and to comprise the water tolerance properties of the oleophilic liquid.

Exemplary demulsifiers which may be employed in the practice of the claimed invention include poly(alkylphenol) formaldehyde condensates and the polyalkyleneoxy modified reaction products thereof. These compounds are prepared by reacting an alkylphenol with formaldehyde and thereafter reacting the reaction product of the above with a C_2 to C_3 alkylene oxide such as ethylene oxide and propylene oxide. The demulsifiers have a generalized structural formula:



wherein

U is an alkylene of 2 to 3 carbons;

y is an integer averaging between 4 and 10;

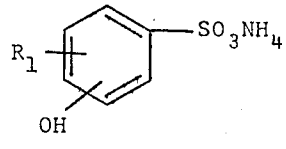
x is an integer averaging between 4 and 10; and

R_5 is an alkyl having from 4 to 15 carbons.

Preferred demulsifiers described by the above formula are polyethyleneoxy modified methylene bridged poly(alkylphenol) polymers having a polyethyleneoxy chain of 8 to 20 carbons and preferably from 10 to 16 carbons and at least about 75 number per cent of the polyethyleneoxy chains being within the range specified. The methylene bridged poly(alkylphenol) portion of the polymer has from 4 to 10 and preferably from 5 to 8 repeating methylene bridged alkylphenol units with 4 to 15 and preferably 6 to 12 carbons in the alkyl group. In preferred embodiments, the alkyl groups is a mixture of alkyls having between 4 and 12 with a number average carbon atom range between 6 and 10.

Illustrative alkylphenols include, p-isobutylphenol, p-diisobutylphenol, p-hexylphenol, p-heptylphenol, p-octylphenol, p-tripropylenephenol, p-dipropylenephenol, etc.

Another type of demulsifier component is an ammonia-neutralized sulfonated alkylphenol. These compounds have the general structure:



wherein R_1 is a hydrocarbyl having from 4 to 15 carbons, preferably from 6 to 12.

These compounds are prepared by sulfonating an alkylated phenol and thereafter neutralizing the sulfonated product with ammonia.

Another type of demulsifier is an oxyalkylated glycol. These compounds are prepared by reacting a polyhydroxy alcohol such as ethylene glycol, trimethylene glycol, etc., with ethylene or propylene oxide. Many of the compounds are commercially available from Wyandotte Chemical Company under the Pluronics trademark. They are polyethers terminated by hydroxy groups and produced by the block copolymerization of ethylene oxide and propylene oxide. The ethylene oxide blocks act as the hydrophiles and the propylene oxide blocks as the hydrophobes. They are available in a wide range of molecular weights and with varying ratios of ethylene oxide to propylene oxide blocks.

The above demulsifier components may be employed individually or in mixtures. A particularly active demulsifier is a mixture of 10 to 90 parts of alkoxy-modified, methylene-bridged polyalkylphenol, 10 to 90 parts of ammonia-neutralized sulfonated alkylphenol, and 10 to 90 parts of an oxyalkylated glycol, per 100 parts of total demulsifier employed.

The demulsifier may be added to the rust inhibitor mixture with or without the aid of a solvent. Generally, however, an inert, stable, organic solvent is employed. Exemplary solvents include those recited *infra* under the description of concentrates for the additive mixture.

OLEOPHILIC ORGANIC LIQUID

The oleophilic liquid which can be improved with respect to its rust inhibiting properties encompasses a wide range of stable organic liquids. The term "oleophilic", as employed herein, means oil miscible or having an affinity for fats and oils. Another expression meaning the same as oleophilic is lipophilic or hydrophobic. The oleophilic liquids must also be relatively inert to the rust inhibitors and demulsifier if one is employed.

Typical oleophilic liquids include hydrocarbon oils, fuels, synthetic oils, natural fats and oils, mineral oils, etc. Exemplary oleophilic liquids which may be employed in the practice of this invention are hydrocarbons boiling between about 90° and 1,000°F. and inclusive of fuel oils, furnace or heating oils, gas oils, lubricating oils, diesel oils, stove oils, jet fuels, motor gasoline, organic solvents, kerosene, etc.; synthetic oils such as alkylene polymers, alkylene oxide type polymers, carboxylic acid esters (e.g., those which were prepared by esterifying carboxylic acids such as adipic acid, azelaic acid, suberic acid, sebacic acid, alkenyl succinic acid, fumaric acid, maleic acid, etc. with an alcohol such as butyl alcohol, hexyl alcohol, 2-ethylhexyl alcohol, pentacrythritol, etc), etc.

The particularly preferred oleophilic liquids are hydrocarbon oils boiling between about 300° and 750°F.

The oleophilic liquid having the improved properties is prepared by simply admixing therein the inhibitor mixture and other additives as are necessary. Normally, the inhibitor mixture is prepared within an organic solvent medium. This solvent may be removed prior to its addition to the oleophilic liquid by conventional means such as distillation, extraction, precipitation, etc. In most instances, however, the presence of the organic solvent within the oleophilic liquid does not adversely affect the liquids properties. In these instances the solvent is admixed with the oleophilic liquid along with the inhibitor mixture.

The concentration of the inhibitor mixture and other additives within the oleophilic liquid sufficient to impart the desired properties depends upon the additive selected, the oleophilic liquid used, the amount of water present within the system, the temperatures involved, the metal storage tanks and vessels involved,

etc. Generally, however, the components will be present in the amounts shown in the following Table 1.

TABLE 1

Component	COMPONENT CONCENTRATION Broad Range	Preferred Range
1.Oleophilic liquid (Wt. %)	Major Portion	99-~100
2.Inhibitor Mixture		
a.Copolymer (ppm)	25-500	50-75
b.Hydrocarbyl amine, amide, imidazoline or mixtures thereof (ppm)	10-500	35-50
3.Demulsifier (ppm)	0-25	0.1-10
4.Other Additives (ppm)	0-2000	10-500

The ratio of α-olefin-maleimide copolymer to the hydrocarbyl amine, amide or imidazoline present within the inhibitor mixture will generally be within the range of 10 to 0.75 parts of copolymer per part of amine, and preferably from 2 to 4 parts copolymer per part of amine. The amount of demulsifier will likewise vary depending upon the amounts of inhibitor mixture present. Generally, the demulsifier is present between about 1 and 5 parts, and probably between 1 and 2 parts per 100 parts of inhibitor mixture.

Concentrates of the inhibitor mixture can be made and provides a convenient means for transporting and storing the mixture without the necessity of very large storage tanks and vessels. When concentrates are employed, they may be transported to the site where blending of various additives is performed and simply blended or admixed with the oleophilic liquid. The concentrates generally contain from 50 to 100 weight percent, and preferably from 50 to 60 weight percent of the inhibitor mixture at the ratios above-described in a suitable organic solvent. Typically, the organic solvent is composed of the oleophilic liquid above mentioned, although other organic inert, stable solvents may be employed. Exemplary solvents include aliphatic and aromatic hydrocarbons, aliphatic ethers, halogenated hydrocarbons, and preferably mixed aromatics (i.e., xylenes from reformate fractions) or aliphatics boiling within the range of 300°-700°F. Other additives of the type mentioned supra may also be present within the concentrate in proportionately greater concentrations as recited in Table 1.

The following examples of specific embodiments of the practice of this invention are presented and should not be understood as limiting the claimed invention, as defined in the accompanying claims.

EXAMPLE 1

This example is presented to illustrate the preparation of a preferred α-olefin-maleimide copolymer which comprises one compound of the inhibitor mixture of this invention.

Into a reaction flask is introduced 243 g. (1.0 mole) of C_{15-20} cracked wax α-olefins*, 98 g. (1.0 mole) of maleic anhydride and 341 g. of benzene. The mixture is stirred at a temperature of 140°F., and 9.7 g. (0.04 mole) of benzoyl peroxide in a minimum of benzene is added. The solution is then heated at 185°F. for 12 hours. The reaction product is recovered by precipitation with methanol and redissolved in benzene. The yield is 290 grams (85%).

*C_{15-20}

No. of Carbon Atoms	Mole %
14	1
15	12
16	19
17	18
18	18
19	17
20	14
21	1
1-olefin	94
straight chain	86

Into another reaction flask is introduced 341 g. (1.0 gram equivalent based on anhydride groups) of a 50.0 weight percent solution of the copolymer prepared above in benzene, 324 g. (1.0 mole) of N-(aminopropyl) oleylamine and 306 g. of xylene. The mixture is stirred at a temperature of 356°F. for 6 hours at which time approximately 18 g. of water is collected in a trap. The mixture is then filtered through Celite. The yield is 582 g. (90%). The product is characterized by its infrared spectrum, showing the characteristic succinimide absorption. The molecular weight of the copolymer, as measured by (ThermoNAM), is 6,140.

EXAMPLE 2

This example is presented to illustrate the effectiveness of the inhibitor mixture in suppressing rust formation in storage tanks containing a fuel oil. The example also illustrates the improvement of the inhibitor mixture over the mixture's components when used individually and over the employment of no inhibitor.

In each of the experiments, 100 gallons of a test hydrofined heating fuel oil boiling between about 300° and 550°F. is charged into a new 110-gallon steel storage tank. One liter of distilled water is then added to the tank. The test fuel oil is circulated 8 hours a day for 16 weeks through copper tubing, cotton filters, Webster pump and back to the tank. Once each month during the 16 week test period, the water bottoms and test fuel in each tank are agitated for 1 minute with compressed nitrogen to simulate tank filling. At the end of the 16 week test period, the fuel and water are drawn off and the tanks washed and cut in half for observation.

The tank rust is visually observed and rated in accordance with the rating schedule set forth in the following Table 2.

TABLE 2

Visual Observation	RATING SCHEDULE Rating
1. No rust — metal bright	1
2. Metal stained — no rust	2
3. Isolated rust spots	3
4. Minor rust cover, less than 5%	4
5. Rust cover, 5-10%	5
6. Rust cover, 10-50%	6
7. Rust cover, 50-80%	7
8. Rust cover, 80-90% of surface	8
9. Severe rust cover, 100% of surface	9
10. Severe corrosion pitting	10

Three storage tanks are employed in this example along with three different test fuel oils. One test oil contains no additive and is designated as the "no additive"

test oil. Another test oil contains 100 parts per million of N-(aminopropyl) oleylamine and this oil is designed as the "hydrocarbyl amine only" test oil. The third test oil contains 50 parts per million of the hydrocarbyl amine and 150 ppm of a solution consisting of 12 wt. % n-butanol, 1% of a standard demulsifier, 43.5 wt. % of the copolymer prepared by the method of Example 1 and 43.5 wt. % of an aromatic solvent. This third test oil is designated as the "inhibitor mixture" test oil.

The results from the 16 week rust experiments with the above test oils are presented below in Table 3.

TABLE 3

16 WEEK STORAGE TANK RUST TESTS Test Oil	Rating
1. No additive	8
2. Hydrocarbylamine only	5
3. Inhibitor mixture	3

The above Table illustrates an improvement of 2 points on the rating scale from utilizing the mixture of components rather than the hydrocarbyl amine alone and an improvement of 5 points over the fuel containing no inhibitor.

EXAMPLE 3

The test procedure of Example 2 is repeated with identical test oils except that one liter of sea water is employed in place of the distilled water. At the end of the 16 week storage tank rust test, the following results are observed and reported in Table 4.

TABLE 4

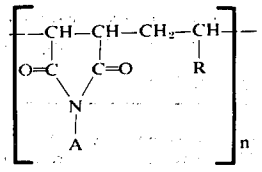
16 WEEK STORAGE TANK RUST TESTS Test Oil	Rating
1. No additive	10
2. Hydrocarbylamine only	8
3. Inhibitor mixture	6

The above Table again illustrates an improvement of 2 points on the rating scale from utilizing the mixture of components rather than the hydrocarbylamine alone, and an improvement of 4 points over the fuel containing no inhibitor.

I claim:

1. A composition of matter comprising in an admixture (1) a copolymer of an alpha-olefin having from 8 to 30 carbons and an N-substituted maleimide wherein the N-substituents are organic radicals having from 3 to 60 carbons and from 1 to 5 amine nitrogens, said copolymer having from 4 to 20 repeating olefin-maleimide units, and (2) a hydrocarbyl amine, having from 3 to 60 carbons and from 1 to 10 nitrogens, the ratio of said copolymer to said hydrocarbyl amine, being within the range of 10 to 0.75 parts of copolymer per part of hydrocarbyl amine.

2. The composition defined in claim **1** wherein said copolymers have as the repeating group, a unit of the following general structure:



wherein

A is an aliphatic organic radical of 3 to 60 carbons and 1 to 5 nitrogens;

R is a hydrocarbyl having from 6 to 28 carbons; and

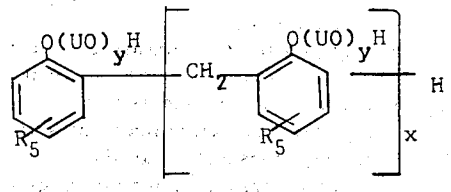
n is an integer from 4 to 20.

3. The composition defined in claim **2** wherein said hydrocarbyl amine, is N-(aminopropyl)oleylamine.

4. The composition defined in claim **2** wherein a demulsifier is also present within said admixture.

5. The composition defined in claim **4** wherein said demulsifier is selected from the group consisting of (1) an alkoxy-modified methylene-bridged-polyalkyl phenol, (2) an ammonia neutralized sulfonated alkyl phenol, (3) an oxyalkylated glycol, and (4) mixtures thereof.

6. The composition defined in claim **4** wherein said demulsifier has the following generalized structural formula:



wherein

U is an alkylene of 2 to 3 carbons;

y is an integer from 4 to 10;

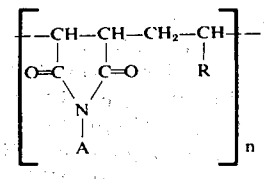
x is an integer from 4 to 10; and

R_5 is an alkyl having from 4 to 15 carbons.

7. A composition of matter comprising in an admixture (1) a major amount of an oleophilic organic liquid, (2) from 25 to 500 weight parts per million of a copolymer of an alpha-olefin having from 8 to 30 carbons and an N-substituted maleimide wherein the N-substituents are organic radicals having from 3 to 60 carbons and from 1 to 5 nitrogens, said copolymer having from 4 to 20 repeating olefin-maleimide units, and (3) from 10 to 500 weight parts per million of a hydrocarbyl amine, having from 3 to 60 carbons and from 1 to 10 nitrogens with a carbon to nitrogen atomic ratio from 5 to 30:1.

8. The composition defined in claim **7** wherein said oleophilic liquid is a petroleum distillate fuel.

9. The composition defined in claim **8** wherein said copolymers have as the repeating group, a unit of the following general structure:



wherein

A is an aliphatic organic radical of 3 to 60 carbons

and 1 to 5 amine nitrogens;

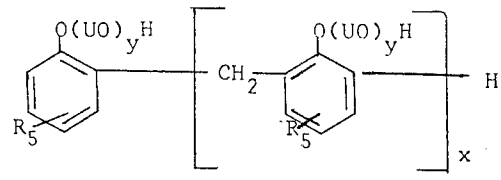
R is a hydrocarbyl having from 6 to 28 carbons; and

n is an integer from 4 to 20.

10. The composition defined in claim **9** wherein a demulsifier is also present within said admixture.

11. The composition defined in claim **10** wherein said demulsifier is selected from the group consisting of (1) an alkoxy-modified methylene-bridged-polyalkyl phenol, (2) an ammonia neutralized sulfonated alkyl phenol, (3) an oxyalkylated glycol, and (4) mixtures thereof.

12. The composition defined in claim **10** wherein said demulsifier has the following generalized structural formula:



wherein

U is an alkylene of 2 to 3 carbons;

y is an integer from 4 to 10;

x is an integer from 4 to 10; and

R_5 is an alkyl having from 4 to 15 carbons.

13. The composition defined in claim **8** wherein said hydrocarbyl amine, is N-(aminopropyl)-oleylamine.

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