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STABILIZED MINERAL OIL COMPOSITIONS

Paul Y. C. Gee, Woodbury, and Harry J. Andress, Jr., Pitman, N.J., assignors to Socony Mobil Oil Company, Inc., a corporation of New York

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This invention relates to stabilized mineral oil compositions and, more particularly, to mineral oil compositions adapted for use as fuel oils containing certain additives to inhibit the presence of sediment during prolonged periods of storage and to prevent screen-clogging and rusting of ferrous metal surfaces. The invention, furthermore, relates to mineral oil compositions adapted for use as lubricating oils containing the aforementioned additives as rust-inhibitors, which, aside from imparting such desired properties to fuel oils and lubricating oils, also inhibit such fuel oils and lubricating oils against undesirable emulsification.

It is well known to those skilled in the art that the aforementioned fuel oils are prone to form sludge or sediment during prolonged periods of storage. The formation of such sediment has an adverse effect on burner operation, by reason of its tendency to clog screens and nozzles. In addition to sediment, which is formed during storage, most fuel oils contain other impurities, such as rust, dirt and entrained water. Such impurities tend to settle out on equipment parts, such as nozzles, screens, filters and other parts, thereby also clogging them and causing the equipment to fail or perform unsatisfactorily. Another factor, incident to the storage and handling of fuel oils, is the "breathing" of storage vessels. This condition results in the accumulation of considerable quantities of water in the tank or fuels, which creates rusting problems. Thereafter, when the oil is removed for transportation such large amounts of water may be carried along as to cause rusting of ferrous metal surfaces in pipelines, tankers and the like.

In the past, it has been the practice to overcome the aforementioned difficulties by employing a separate additive for each condition encountered, i.e., a sediment inhibitor, an anti-screen clogging agent and an anti-rust agent. The use of several additives, however, results in problems of additive compatibility, thus restricting the choice of additive combinations. In addition, the use of a plurality of additives tends to unduly increase the cost of the fuel.

It is also well known to those skilled in the art that the rusting of ferrous metal surfaces has long been a common occurrence in the field of lubrication, and particularly so in steam turbine lubrication during the initial operation of new installations. Rusting is most pronounced at points where the clearance between bearing surfaces is very small, as for example, in governor mechanisms. This is usually caused by water entering the oil supply, as a result of condensation and entrainment in the oil throughout the circulating system, and thus coming into contact with the ferrous metal surfaces. As in the case of fuel oils, emulsification of the oil is also objectionable in lubricating oils, and, in the case of turbine lubricating oils, is particularly objectionable in that the desired degree of lubrication for metal parts in contact with the emulsified oil, is reduced.

It is, therefore, an object of the present invention to provide a new class of additives for incorporation in mineral oil compositions which are useful as fuel oils and lubricating oils, obviating the disadvantages heretofore encountered in compositions of this type.

Another object of the invention is to provide new and improved stabilized mineral oil compositions containing

the aforementioned additives, and which are useful as fuel oils and lubricating oils.

Other objects and advantages inherent in the invention will become apparent to those skilled in the art from the following detailed description.

It has now been found that the aforementioned problems heretofore encountered in the use of mineral oil compositions, such as fuel oils and lubricating oils, can be obviated by the use of a single additive composition. In general, as more fully hereinafter disclosed, the present invention relates to mineral oil compositions containing a small amount, sufficient to provide the aforementioned improvements, of a metal salt of itaconamic acid and a mixture of aliphatic hydrocarbyl primary branched-chain amines having from about 4 to about 30 carbon atoms per molecule.

The aforementioned mixtures of aliphatic hydrocarbyl primary branched-chain amines having about 4 to about 30 carbon atoms per molecule employed in forming the metal salts of itaconamic acid therewith, comprise, in general, the tertiary-alkyl primary mono-amines in which a carbon atom of a tertiary-alkyl group is attached to the amino group and which have from about 4 to about 30 carbon atoms, and preferably from about 12 to about 24 carbon atoms, per molecule. Thus, these amines contain the group:



Non-limiting examples of these amine reactants are

t-Butyl amine,
t-Hexayl primary amine,
t-Octyl primary amine,
t-Decyl primary amine,
t-Dodecyl primary amine,
t-Tetradecyl primary amine,
t-Octadecyl primary amine,
t-Eicosyl primary amine,
t-Docosyl primary amine,
t-Tetracosyl primary amine, and
t-Triacontyl primary amine.

The amine reactants can be prepared in several ways well known to those skilled in the art. The metal of the metal salts of the additive compositions of the present invention, is a divalent metal, and, preferably, includes magnesium, barium, calcium, zinc and strontium, although other divalent metals may also be employed.

The metal salts are prepared, in general, by first reacting one mole of the aforementioned aliphatic primary amines with one mole itaconic acid at a temperature within the range from about 135° C. to about 185° C., for a period of from about 2 to about 4 hours with the elimination of one mole of water. The resulting amine amic acid is next heated with the appropriate divalent metal (e.g., a Group II metal), in the form of a metal alkoxide, or metal hydroxide, or, if so desired, by the use of an alkali metal hydroxide and double displacement with, for example, a Group II metal halide, (e.g., zinc chloride). The normal metal salts are prepared by heating two moles of the aforementioned amine amic acid with one mole of the metal alkoxide or metal hydroxide, for example, magnesium methoxide or magnesium hydroxide. The alkoxy metal salts are prepared by heating one mole of the aforementioned amine amic acids with one mole of metal alkoxide, for example, magnesium methoxide.

The fuel oils that are improved in accordance with this invention are hydrocarbon fractions having an initial boiling point of at least about 100° F. and an end boiling point no higher than about 750° F., and boiling substan-

tially continuously throughout their distillation range. Such fuel oils are generally known as distillate fuel oils. It is to be understood, however, that this term is not restricted to straight-run distillate fractions. The distillate fuel oils can be straight-run distillate fuel oils, catalytically or thermally cracked (including hydrocracked) distillate fuel oils, or mixtures of straight-run distillate fuel oils, naphthas and the like with cracked distillate stocks. Moreover, such fuel oils can be treated in accordance with well known commercial methods, such as, acid or caustic treatment, hydrogenation, solvent refining, clay treatment, etc.

The distillate fuel oils are characterized by their relatively low viscosities, pour points, and the like. The principal property which characterizes the contemplated hydrocarbons, however, is the distillation range. As mentioned hereinbefore, this range will lie between about 100° F. and about 750° F. Obviously, the distillation range of each individual fuel oil will cover a narrower boiling range falling, nevertheless, within the above-specified limits. Likewise, each fuel oil will boil substantially continuously throughout its distillation range.

Particularly contemplated among the fuel oils are Nos. 1, 2, and 3 fuel oils used in heating and as diesel fuel oils, and the jet combustion fuels. The domestic fuel oils generally conform to the specifications set forth in ASTM Specifications D–396–48T. Specifications for diesel fuels are defined in ASTM Specifications D–975–48T. Typical jet fuels are defined in Military Specification MIL–F–5624B. The amount of the metal salt of itaconamic acid and the aforementioned amines that is added to the distillate fuel oil in accordance with this invention will depend, of course, upon the intended purpose and the particular metal salt selected, as they are not all equivalent in their activities. Some may have to be used in greater concentrations than others to be effective. In most cases, in which it is desired to obtain all of the aforesaid beneficial results, additive concentrations varying between 10 pounds per thousand barrels of oil will be employed. It may not always be desired, however, to accomplish all of the aforementioned results. In such cases, where it is desired to effect only one or two results, lower concentrations can be used. Thus, if it is desired only to prevent rust under dynamic conditions, as in a pipeline, it has been found that concentrations as low as about 5 p.p.m., i.e., about one pound of additive per thousand barrels of oil, are effective. In general, therefore, the amount of metal salt of itaconamic acid and the aforementioned amines that can be added to the distillate fuel oil, in order to achieve a beneficial result, will vary generally between about one pound per thousand barrels of oil and about 200 pounds per thousand barrels of oil. Preferably, it will vary between about 10 and about 200 pounds per thousand barrels of oil.

If it is desired, the fuel oil compositions can contain other additives for the purpose of achieving other results. Thus, for example, there can be present foam inhibitors and ignition and burning quality improvers. Examples of such additives are silicones, dinitropropane, amyl nitrate, metal sulfonates, and the like.

In reference to the aspect of this invention relating to lubricating oils, the additives embodied for use are effective to impart anti-rust properties while also inhibiting emulsification and, particularly, to impart such properties to highly refined mineral lubricating oils for use in steam turbines. For such usage, the additives embodied herein can be used in amounts that can vary over a rather wide range, based on the weight of the lubricating oil but, generally, in an amount of from about 0.001 to about ten percent and, preferably, between about 0.05 and about one percent. If desired, other substances can be added to the lubricating oil to impart other properties and, for example, anti-oxidants pour point depressants, V.I. improvers, extreme pressure agents, etc.

Thus, the improving agents of this invention are useful for various petroleum fractions in concentrations ranging from about 0.001% up to about ten percent based on the weight of the fraction, with the actual concentration used being dependent on the particular oil fraction (fuel oil or lubricating oil) and the use for which the improving agent is intended.

The following specific examples are for the purpose of illustrating the mineral oil compositions of this invention, and of exemplifying the specific nature thereof. It is to be strictly understood, however, that this invention is not to be limited by the particular additives and mineral oils, or to the operations and manipulations described therein. Other salts of itaconamic acid and other amines of the aforementioned types, as well as other mineral oils, as discussed hereinbefore, can be used as those skilled in the art will readily appreciate.

The amine reactants, Primene 81R and Primene JMT, used in the specific working examples 1 through 9 are mixtures of pure amines. Primene 81R is a mixture of primary amines having a carbon atom of a tertiary alkyl group attached to the amino ($-NH_2$) group and containing 12 to 15 carbon atoms per amine molecule. This mixture contains, by weight, about 85 percent tertiary-dodecyl primary amine, about 10 percent tertiary-pentadecyl primary amine, and relative small amounts, i.e., less than 5 percent of amines having less than 12 or more than 15 carbon atoms. Primene JMT is a mixture of tertiary-alkyl primary amines containing 18 to 24 carbons, having a tertiary carbon atom attached to the $-NH_2$ group, and containing, by weight, about 40 percent tertiary octadecyl primary amine, about 30 percent tertiary-eicosyl primary amine, about 15 percent tertiary-docosyl primary amine, about 10 percent tertiary-tetracosyl primary amine, and a small amount, less than 5 percent, and other amines as high as tertiary-triacontyl primary amine. In Example 10 there is shown that the metal salts of itaconamic acid prepared from primary straight-chain amines (rather than from the primary branched-chain amines of the present invention) are unsatisfactory as fuel adidtives, since they are found to develop undesirable, heavy emulsions with water in fuels; whereas the metal salts of the primary branched-chain itaconamic acids of the present invention do not form such emulsions. In Example 10, Armeen S is a mixture of primary straight-chain amines containing, approximately, by weight, 10 percent hexadecylamine, 10 percent octadecylamine, 35 percent octadecenylamine, and 45 percent octadecadienylamine.

Example 1

A mixture of 65 gms. (0.5 mole) of itaconic acid, 100 gms. (0.5 mole) of Primene 81R and 162 gms. of xylene as a diluent was refluxed at 135–145° C. for 3 hours to form the Primene 81R itaconamic acid. The amount of water collected was 10 cc., theory 9 cc. The Primene 81R itaconamic acid was then aded at room temperature, with stirring, to 6.08 gms. (0.25 mole) of magnesium in the form of a magnesium methylate solution. The mixture was gradually heated to 135° C. to distill out the methanol. The reaction product being viscous, was diluted with 162 gms. of xylene and filtered through Hyflo clay. The final product, the magnesium salt of Primene 81R itaconamic acid, which contained 66⅔% xylene, was clear and fluid at room temperature.

Analysis, Percent	Estimated	Found
Mg	1.2	1.37
N	1.4	1.56

Example 2

A mixture of 65 gms. (0.5 mole) of itaconic acid, 150 gms. (0.5 mole) of Primene JMT, 424 gms. of Process oil #5 (a conventional paraffin oil having a viscosity of

100 S.U.S. at 100° F.) and 75 cc. of benzene as a diluent, was refluxed at 135–140° C. for 3 hours to form the Primene JMT itaconamic acid. The amount of water collected was 10 cc., theory 9 cc. The Primene JMT itaconamic acid was then added at room temperature with stirring to 6.08 gms. (0.25 mole) of magnesium in the form of a magnesium methylate solution. The mixture was heated gradually to 140° C. to distill out the methanol. The reaction product was filtered through Hyflo clay. The final product, the magnesium salt of Primene JMT itaconamic acid, which contained 66⅔% Process oil, was clear and fluid at room temperature.

Analysis, Percent	Estimated	Found
Mg	0.94	0.99
N	1.1	1.04

Example 3

A mixture of 65 gms. (0.5 mole) of itaconic acid, 100 gms. (0.5 mole) of Primene 81R, 380 gms. of xylene and 20 cc. of benzene was refluxed at 130–140° C. for 3 hours to form the Primene 81R itaconamic acid. The amount of water collected was 10 cc., theory 9 cc. To the Primene 81R itaconamic acid was added at room temperature with stirring 34.34 gms. (0.25 mole) of barium in the form of a barium methylate solution. The mixture was gradually heated to 135° C. to distill out the methanol. The reaction product was filtered through Hyflo clay. The final product, the barium salt of Primene 81R itaconamic acid, which contained 66⅔% xylene, was clear and fluid at room temperature.

Analysis, Percent	Estimated	Found
Ba	6.0	6.89
N	1.2	1.42

Example 4

A mixture of 43.3 gms. (⅓ mole) of itaconic acid, 100 gms. (⅓ mole) of Primene JMT, 344 gms. of Process oil #5 and 75 cc. of benzene was refluxed at 134–140° C. for 4 hours to form the Primene JMT itaconamic acid. The amount of water collected was 7 cc., theory 6 cc. To the Primene JMT itaconamic acid was added at room temperature with stirring 22.9 gms. (⅙ mole) of barium in the form of a barium methylate solution. The mixture was gradually heated to 135° C. to distill out the methanol. The reaction product was filtered through Hyflo clay. The final product, the barium salt of Primene JMT itaconamic acid, which contained 66⅔% Process oil #5, was clear and fluid at room temperature.

Analysis, Percent	Estimated	Found
Ba	4.6	4.74
N	0.94	0.86

Example 5

A mixture of 65 gms. (0.5 mole) of itaconic acid, 100 gms. (0.5 mole) of Primene 81R and 150 cc. of xylene as diluent was refluxed at 135–145° C. for 3 hours to form the Primene 81R itaconamic acid. To the Primene 81R itaconamic acid was added at room temperature with stirring 20 gms. (0.5 mole) of NaOH previously dissolved in 200 cc. of methanol. The mixture was gradually heated to 140° C. to form a sodium salt. To the sodium salt was added at room temperature with stirring 37.4 gms. (0.25 mole+3.4 gms.) of zinc chloride previously dissolved in 200 cc. of methanol. The mixture was gradually heated to 140° C. and was held at 140° C. for one hour to insure the complete formation of the zinc salt. The reaction product was diluted with 500 cc. of benzene, filtered through Hyflo clay and distilled to 150° C. under house vacuum. The residue, the zinc salt of Primene 81R itaconamic acid, which weighed 154 gms., theory 171 gms., being viscous was diluted with 158 gms. of xylene.

Analysis, Percent	Estimated	Found
Zn	5.2	4.84
N	2.1	2.21

Example 6

A mixture of 65 gms. (0.5 mole) of itaconic acid, 150 gms. (0.5 mole) of Primene JMT, 221 gms. of Process oil #5, and 100 cc. of toluene was refluxed at 135–145° C. for 3 hours to form the Primene JMT itaconamic acid. The amount of water collected was 9 cc., theory 9 cc. To the Primene JMT itaconamic acid was added at room temperature with stirring 20 gms. (0.5 mole) of sodium hydroxide, previously dissolved in 300 cc. of methanol. The mixture was gradually heated to 150° C. to form a sodium salt. To the sodium salt was added at room temperature, with stirring 37.4 gms. (0.25 mole+3.4 gms. excess) of zinc chloride, previously dissolved in 300 cc. of methanol. The mixture was gradually heated to 150° C. and held at 150° C. for one hour. The reaction product was permitted to settle and filtered through Hyflo clay. The final product, the zinc salt of Primene JMT itaconamic acid, which contained 50% Process oil #5, was clear and fluid at room temperature.

Analysis, Percent	Estimated	Found
Zn	3.6	3.34
N	1.5	1.58

Example 7

A mixture of 65 gms. (0.5 mole) of itaconic acid, 100 gms. (0.5 mole) of Primene 81R and 100 cc. of toluene, as diluent was refluxed at 135° C. for 3 hours to form the Primene 81R itaconamic acid. The amount of water collected was 10 cc., theory 9 cc. To the Primene 81R itaconamic acid was added at room temperature with stirring 20 gms. (0.5 mole) of sodium hydroxide, previously dissolved in 300 cc. of methanol. The mixture was gradually heated to 150° C. to form a sodium salt. The sodium salt was diluted with 165 gms. of xylene. To the sodium salt was added at room temperature with stirring 29.2 gms. (0.25 mole+1.45 gms. excess) of $CaCl_2$ previously dissolved in 300 cc. of methanol. The mixture was gradualy heated to 130° C. to distil out the methanol. The reaction product was permitted to settle and filtered through Hyflo clay. The final product, the calcium salt of Primene 81R itaconamic acid, which contained approximately, 50% xylene, was clear and fluid at room temperature.

Analysis, Percent	Estimated	Found
Ca	3.0	2.65
N	2.1	1.88

Example 8

A mixture of 65 gms. (0.5 mole) of itaconic acid, 150 gms. (0.5 mole) of Primene JMT, 215 gms. of Process oil #5, and 100 cc. of toluene was refluxed at 135–145° C. for 3 hours to form the Primene JMT itaconamic acid. To the Primene JMT itaconamic acid was added at room temperature with stirring 20 gms. (0.5 mole) of sodium hydroxide, previously dissolved in 300 cc. of methanol. The mixture was gradually heated to 150° C.

to form a sodium salt. To the sodium salt was gradually added at room temperature with stirring 29.2 gms. (0.25 mole+1.45 gms. excess) of calcium chloride previously dissolved in 300 cc. of methanol. The mixture was gradually heated to 175° C. to form a calcium salt and was held at 175° C. for one hour. The reaction product was permitted to settle and filtered through Hyflo clay. The final product, the calcium salt of Primene JMT itaconamic acid, which contained 50% Process oil #5, was clear and fluid at room temperature.

Analysis, Percent	Estimated	Found
Ca	2.3	2.3
N	1.6	1.3

Example 9

A mixture of 32.5 gms. (0.25 mole) of itaconic acid, 75 gms. (0.25 mole) of Primene JMT diluted with 238 gms. of Process oil #5 and 100 cc. of toluene, was refluxed at 135–145° C. for 4 hours to form the Primene JMT itaconamic acid. The Primene JMT itaconamic acid was added at room temperature with stirring to a zinc methylate solution, previously prepared by reacting 11.5 gms. (0.5 mole) of sodium in the form of sodium methylate solution with 36 gms. (0.25 mole+2 gms. excess) of zinc chloride dissolved in 300 cc. of methanol. The mixture, being heated gradually with stirring to distill out the methanol, thickened at 82° C. A quantity of 3.5 cc. of water, added dropwise, made the reaction mixture fluid again. The temperature was gradually raised to 150° C. and was held at 150° C. for one hour. The reaction product was then allowed to settle and filtered through Hyflo clay. The final product, the methoxy zinc salt of Primene JMT itaconamic acid, which contained 66⅔% Process oil #5, was clear and fluid at room temperature.

Analysis, Percent	Estimated	Found
Mg	4.5	4.85
N	0.97	0.88

Example 10

A mixture of 65 gms. (0.5 mole) of itaconic acid, 150 gms. (0.5 mole) of Armeeen S, diluted with 212 gms. of xylene and 50 cc. of benzene was refluxed at 135–145° C. for 3 hours to form the Armeen S itaconamic acid. The amount of water collected was 9 cc., theory 9 cc. The Armeen S itaconamic acid was then added at room temperature, with stirring to 6.08 gms. (0.25 mole) of magnesium in the form of a magnesium methylate solution. The mixture was gradually heated to 135° C. to distill out the methanol. The reaction product was filtered through Hyflo clay. The final product, the magnesium salt of Armeen S itaconamic acid, which contained 66⅔% xylene, was clear and fluid at room temperature.

Analysis, Percent	Estimated	Found
Mg	0.97	1.08
N	1.13	0.97

In the following Table I, data are set forth showing the results obtained by subjecting to the following screen-clogging test, a base fuel oil with and without the addition agents embodied herein.

SCREEN CLOGGING

The anti-screen clogging characteristics of a fuel oil were determined as follows: The test is conducted using a Sundstrand V3 or S1 home fuel oil burner pump with a self-contained 100-mesh Monel metal screen. About 0.05 percent, by weight, of naturally-formed fuel oil sediment, composed of fuel oil, water, dirt, rust, and organic sludge is mixed with 10 liters of the fuel oil. The mixture is circulated by the pump through the screen for 6 hours. Then, the sludge deposit on the screen is washed off with normal pentane and filtered through a tared Gooch crucible. After drying, the material in the Gooch crucible is washed with a 50–50 (volume) acetone-methanol mixture. The total organic sediment is obtained by evaporating the pentane and the acetone-methanol filtrates. Drying and weighing the Gooch crucible yields the amount of inorganic sediment. The sum of the organic and inorganic deposits on the screen can be reported in milligrams recovered or converted into percent screen clogging.

TABLE I.—SCREEN CLOGGING TESTS

[Inhibitors blended in a fuel oil blend comprising 60% catalytically cracked component and 40% straight run component—approximately 320-640° F.boiling range]

Inhibitor	Conc., lb./1,000 bbls.	Screen clogging, percent
Uninhibited fuel blend	0	100
Uninhibited fuel blend plus Ex. 1	50	19
Uninhibited fuel blend plus Ex. 2	50	1
Uninhibited fuel blend plus Ex. 3	25	17
Uninhibited fuel blend plus Ex. 4	25	3
Uninhibited fuel blend plus Ex. 5	25	5
Uninhibited fuel blend plus Ex. 6	50	4
Uninhibited fuel blend plus Ex. 7	25	19
Uninhibited fuel blend plus Ex. 8	25	6
Uninhibited fuel blend plus Ex. 9	50	6

As is apparent from the data in Table I, the addition agents embodied herein are markedly effective for inhibiting the screen-clogging characteristics of fuel oils.

In the following Table II, data are set forth showing the results obtained by subjecting to the following sedimentation test, a base fuel oil with and without the addition agents embodied herein.

SEDIMENTATION

The test used to determine the sedimentation characteristics of the fuel oils is the 110° F. storage test. In this test, a 500-milliliter sample of the fuel oil under test is placed in a converted oven maintained at 110° F. for a period of 12 weeks. Then, the sample is removed from the oven and cooled. The cooled sample is filtered through a tared asbestos filter (Gooch crucible) to remove insoluble matter. The weight of such matter in milligrams is reported as the amount of sediment. A sample of the blank, uninhibited oil is run along with a fuel oil blend under test. The effectiveness of a fuel oil containing an inhibitor is determined by comparing the weight of sediment formed in the inhibitor oil with that formed in the uninhibited oil.

TABLE II.—FUEL OIL STORAGE TESTS

[Inhibitors blended in a fuel oil blend comprising 60% catalytically cracked component and 40% straight run component—approximately 320-640° F boiling range]

Inhibitor	Concn., lb./1,000 bbls.	Sediment mg./liter
Uninhibited fuel blend	0	129
Uninhibited fuel blend plus Ex. 1	50	75
Uninhibited fuel blend	0	129
Uninhibited fuel blend plus Ex. 2	50	72
Uninhibited fuel blend	0	129
Uninhibited fuel blend plus Ex. 4	50	89
Uninhibited fuel blend	0	129
Uninhibited fuel blend plus Ex. 7	50	58
Uninhibited fuel blend	0	129
Uninhibited fuel blend plus Ex. 8	50	66
Uninhibited fuel blend	0	6
Uninhibited fuel blend plus Ex. 9	50	4

As is apparent from the data in Table II, the addition agents, embodied herein inhibit the tendency of fuel oils against sedimentation on prolonged storage.

In the following Tables III and IV, data are shown for, respectively, the results of tests of (a) a fuel oil with and

without the addition agents embodied herein and (b) a light turbine oil with and without the addition agents embodied herein to determine the effectiveness of the addition agents as antirust agents. Such tests were carried out under the conditions of ASTM Rust Test D–665, operated at 48 hours at 80° F., using distilled water.

TABLE III.—ASTM RUST TEST D-665

[Inhibitors blended in a fuel oil blend comprising 60% catalytically cracked component and 40% straight run component—approximately 320–640° F. boiling range]

Inhibitor	Concn., p.p.m.	Rust test result
Blank fuel blend	0	Fail.
Blank fuel blend plus Ex. 1	10	Pass.
Blank fuel blend plus Ex. 2	10	Do.
Blank fuel blend plus Ex. 3	10	Do.
Blank fuel blend plus Ex. 4	10	Do.
Blank fuel blend plus Ex. 5	10	Do.
Blank fuel blend plus Ex. 6	10	Do.
Blank fuel blend plus Ex. 7	10	Do.
Blank fuel blend plus Ex. 8	25	Do.

TABLE IV.—ASTM RUST TEST D-665

[Inhibitors blended in a light turbine oil]

Inhibitors	Concn., wt. percent	Rust test result
Blank light turbine oil	0	Fail.
Blank light turbine oil plus Ex. 2	0.3	Pass.
Blank light turbine oil plus Ex. 4	0.3	Do.
Blank light turbine oil plus Ex. 6	0.2	Do.
Blank light turbine oil plus Ex. 8	0.2	Do.
Blank light turbine oil plus Ex. 9	0.2	Do.

As is apparent from the data in Tables III and IV, the addition agents of this invention effectively inihibited the fuel oils against rusting.

Over and above the aforesaid improvements imparted to mineral oil compositions by the addition agents embodied herein, such addition agents also function as inhibitors against objectionable emulsification. In that respect, the presence of the tertiary carbon atom linked to the nitrogen atom in the alkyl grouping of the metal salts embodied herein is important as, when corresponding metal salts, but in which the nitrogen atom is linked to a normal primary aliphatic group, such salts induce severe emulsification with water. Thus, reference is made to Example 10 showing preparation of a magnesium salt of itaconamic acid derived from Armeen S, which is a mixture of primary straight-chain amines as hereinbefore described. To illustrate the importance of a tertiary carbon atom linked to the nitrogen atom in the additives embodied herein for inhibiting emulsification, fuel oil compositions were prepared by (1) addition of the metal salt of Example 1 at a concentration of 25 lbs./thousand barrels of a fuel oil as used for the aforedescribed fuel oil tests and (2) addition in the same concentration in such a fuel of the metal salt of Example 10, and such fuel oil compositions were subjected to the following emulsion test:

EMULSION TEST

The procedure for the fuel oil emulsion tests is as follows: a 200 milliliter portion of the fuel to be tested and 20 milliliters of distilled water are placed in a clear glass pint bottle. The bottle is tightly capped and set in an Everbach mechanical shaker in a horizontal position such that the maximum degree of agitation is afforded. The shaker is run at its maximum setting for 5 minutes. The bottle is then removed and allowed to stand in an upright position in the dark for 24 hours. At the end of the 24 hours settling period, the appearance of the water layer is noted. The fuel layer is siphoned off, care being taken not to disturb the oil-water interface, and is discarded. A fresh portion of the fuel oil being tested is then added. The described sequence of steps is repeated. If no emulsion appears in the water layer after this sequence has been performed ten times, the oil is considered to have passed the test. On the other hand, if, after any 24 hour settling period in the procedure, there is any degree of emulsification in the water layer, the fuel considered to have failed the test. This test procedure has been found to provide emulsions in inhibited oils similar to emulsions which occur in these same oils only after prolonged periods of normal handling and storage in the field on a commercial basis.

RATING SCALE FOR REPORTING EMULSION TEST RESULTS; DESCRIPTION OF EMULSIONS

Rating:

0 Clean break on the interface of oil and water. No dirt, skin, or bubbles present.

1 Very slight skin at the oil-water interface that usually does not break on tilting the bottle.

2 Skin at oil-water interface, heavier than #1 and usually accompanied with dirt and bubbles on the skin. No evidence of any white emulsion.

3 First sign of white emulsion. Usually forms at the bottom and in the center of the bottle. It is circular in shape and approximately ¼ to 1 inch in diameter.

4 Approximately the same amount of emulsion on the bottom of the bottle as #3. However, emulsion is also beginning to form at oil-water interface and extends 1/32" to 1/16" downward into the water layer. Roughly 15% of water layer occupied by emulsion.

5 Circular emulsion at bottom of bottle extends outward and upward resembling spokes. Emulsion at the interface a little thicker than #4.

6 More emulsion than #5. Thin film of emulsion forming on sides of bottle surrounding the water layer. Water is still visible looking through the sides and looking up from the bottom of the bottle.

7 Emulsion on bottom of water layer is almost solid. Emulsion on sides of bottle is broken in a few spots enabling the operator to see the water layer.

8 Semi-solid emulsion with perforations or bubbles similar to a honeycomb. No water visible except that seen in the bubbles.

9 Same emulsion as #8 but with less bubbles. 75–90% emulsion is solid.

10 Almost completely solid emulsion with only a few air bubbles visible.

11 Completely solid emulsion (Mayonnaise type).

The results obtained from the foregoing emulsion test were as follows:

TABLE V.—EMULSION TEST

[Inhibitors blended in a fuel oil blend comprising 60% catalytically cracked component and 40% straight run component—approximately 320–640° F. boiling range]

Inhibitor	Concn., lb./1,000 bbls.	Test result
Uninhibited fuel blend plus Ex. 1	25	1
Uninhibited fuel blend plus Ex. 10	25	10

It is apparent from the foregoing that the magnesium salt of Primene 81R itaconamic acid (Ex. 1) containing a tertiary carbon atom attached to the nitrogen atom effectively inhibited emulsification (Rating 1), whereas the corresponding magnesium salt (Ex. 10), but prepared from primary straight-chain amines (Armeen S), resulted in a composition that emulsified severely (Rating 10).

Although the present invention has been described with preferred embodiments, it is to be understood that various modifications and adaptations thereof may be resorted to, without departing from the spirit and scope of this

invention, as those skilled in the art will readily understand.

We claim:

1. A liquid mineral oil containing a small amount sufficient to inhibit corrosion of said oil of a divalent metal salt of the reaction product of itaconic acid and a mixture of aliphatic hydrocarbyl primary branched-chain amines having from about 4 to about 30 carbon atoms per molecule.

2. A composition as defined in claim 1, wherein the mineral oil is a distillate fuel oil.

3. A composition as defined in claim 1, wherein the mineral oil is a lubricating oil.

4. A composition as defined in claim 1, wherein the metal is a divalent metal of the group consisting of magnesium, barium, calcium, zinc and strontium.

5. A composition as defined in claim 1, wherein the mineral oil is a distillate fuel oil having an initial boiling point of at least about 100° F. and an end boiling point not higher than about 750° F. and boiling substantially continuously throughout its distillation range.

6. A liquid mineral oil containing from about 1 to about 200 pounds, per thousand barrels of said oil, a divalent metal salt of the reaction product of itaconic acid and a mixture of aliphatic hydrocarbyl primary branched-chain amines having from about 4 to about 30 carbon atoms per molecule.

7. A liquid mineral oil containing from about 1 to about 200 pounds, per thousand barrels of said oil, of a divalent metal salt of the reaction product of itaconic acid and a mixture of primary amines having a carbon atom of a tertiary alkyl group attached to the amino group and having from about 12 to about 24 carbon atoms per amine molecule.

8. A liquid mineral oil containing from about 1 to about 200 pounds, per thousand barrels of said oil, of a divalent metal salt of the reaction product of itaconic acid and a mixture of primary amines having a carbon atom of a tertiary alkyl group attached to the amino group and having from about 12 to about 15 carbon atoms per amine molecule.

9. A liquid mineral oil containing from about 1 to about 200 pounds, per thousand barrels of said oil, of a divalent metal salt of the reaction product of itaconic acid and a mixture of primary amines having a carbon atom of a tertiary alkyl group attached to the amino group and having from about 18 to about 24 carbon atoms per amine molecule.

10. A divalent metal salt of the reaction product of itaconic acid and a mixture of aliphatic hydrocarbyl primary branched-chain amines having from about 4 to about 30 carbon atoms per molecule.

11. The compound of claim 10 wherein the metal is a divalent metal of the group consisting of magnesium, barium, calcium, zinc and strontium.

12. A divalent metal salt of the reaction product of itaconic acid and a mixture of primary amines having a carbon atom of a tertiary alkyl group attached to the amino group and having from about 12 to about 24 carbon atoms per amine molecule.

13. A divalent metal salt of the reaction product of itaconic acid and a mixture of primary amines having a carbon atom of a tertiary alkyl group attached to the amino group and having from about 12 to about 15 carbon atoms per amine molecule.

14. A divalent metal salt of the reaction product of itaconic acid and a mixture of primary amines having a carbon atom of a tertiary alkyl group attached to the amino group and having from about 18 to about 24 carbon atoms per amine molecule.

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DANIEL E. WYMAN, *Primary Examiner.*

C. F. DEES, *Assistant Examiner.*