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MINERAL OIL COMPOSITIONS CONTAINING METAL SALTS OF CITRAMIC ACIDS

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This invention relates to the improvement of liquid petroleum fractions and, more particularly, to mineral oil compositions adapted for use as fuel oils containing certain additives adapted to inhibit the appearance of sediment during prolonged storage periods, to prevent screen-clogging, and to prevent rusting of ferrous metal surfaces, and to mineral oil compositions adapted for use as lubricating oils containing such additives as rust inhibitors and which, while imparting such desired properties to fuel oils and lubricating oils, also inhibits such fuel oils and lubricating oils against objectionable emulsification.

It is well known that fuel oils are prone to form sludge or sediment during periods of prolonged storage. This sediment, of course, has an adverse effect on burner operation because it has a tendency to clog screens and nozzles. In addition to sediment formed during storage, most fuel oils contain other impurities, such as rust, dirt, and entrained water. The sediment and impurities tend to settle out on equipment parts, such as nozzles, screens, filters, etc., thereby clogging them and causing the equipment to fail. A further factor, incident to the storage and handling of fuel oils, is the "breathing" of storage vessels. This results in the accumulation of considerable amounts of water in the tanks, which presents a problem of rusting in the tanks. Then, when the oil is removed for transportation, sufficient water may be carried along to cause rusting of ferrous metal surfaces in pipelines, tankers and the like.

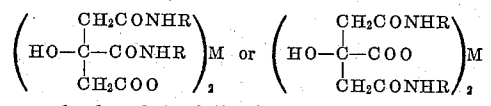
Generally, it has been the practice to overcome the afore-described difficulties with fuel oils with a separate additive for each purpose, i.e., with a sediment inhibitor, an anti-screen clogging agent, and an antirust agent. The use of several additives, however, gives rise to problems of additive compatability, thus restricting the choice of additive combinations. In addition, the use of a plurality of additives unduly increases the cost of the fuel.

As is also well known to those skilled in the art, the rusting of ferrous metal surfaces has been a common occurrence in the field of lubrication and, particularly, 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 in governor mechanism, and is usually caused by water entering the oil supply, as by condensation and entrainment in the oil throughout the circulating system, thereby 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 is reduced for metal parts in contact with emulsified oil.

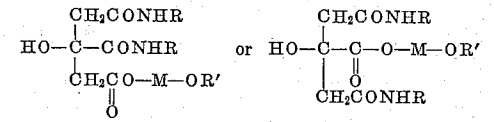
It has now been found that all such problems encountered with mineral oil compositions, such as fuel oils and lubricating oils, are obviated by the use of a single fuel oil addition agent in the form of certain metal salts of partial amides of citric acid.

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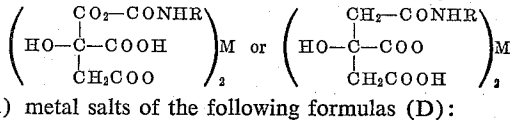
In general, the present invention relates to mineral oil compositions containing a small amount, sufficient to provide the aforesaid improvements, of a compound selected from the group consisting of (a) metal salts of the following formulas (A):



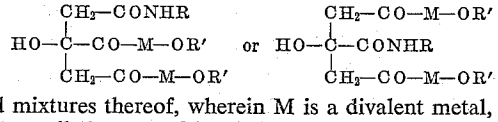
(b) metal salts of the following formulas (B):



(c) metal salts of the following formulas (C):



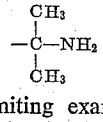
(d) metal salts of the following formulas (D):



and mixtures thereof, wherein M is a divalent metal, and R is an alkyl group of from about 4 to about 30 and preferably about 12 to 24 carbon atoms and having a tertiary carbon atom attached to the nitrogen atom, and R′ is alkyl. In such salts, the metal component M is, preferably, a metal from the group consisting of magnesium, barium, calcium and zinc but, if desired, the metal M can be another metal (e.g., strontium) from group II of the Periodic Table. The alkyl group R′ is, preferably, a lower molecular weight alkyl group and, for example, containing from about 1 to about 18 carbon atoms and, more preferable, a methyl group.

The citramic acids that can be used for preparation of such metal salts can be made by any of the methods known in the art for preparing such compounds and, for example, by heating two moles of an appropriate aliphatic primary amine with one mole of citric acid monohydrate at 150–165° C. for from 2 to 6 hours with elimination of three moles of water to form the diamide of citric acid; and by heating, at 135–145° C. for about three hours, one mole of the appropriate aliphatic primary amine with one mole of citric acid monohydrate to form the monoamide of citric acid.

The amines utilizable in forming the citramic acids are the tertiary-alkyl primary mono-amines in which a primary amino group (—NH_2) is attached to a tertiary carbon atom of an alkyl group of between 4 and 30 carbon atoms. Thus, the amines contain the group:



and of which non-limiting examples include t-dodecyl primary amine, t-tetradecyl primary amine, t-pentadecyl primary amine, t-hexadecyl primary amine, t-octadecyl primary amine, t-eicosyl primary amine, t-tetracosyl primary amine, and t-triacontyl primary amine. Mixtures of such amines can also be used. The use of amines containing such a tertiary carbon atom group, whereby

the group R in the foregoing formulas is an alkyl group having a tertiary carbon atom attached to the nitrogen atom of the metal salts of the citramic acid, is of substantial importance as it provides such metal salts of citramic acid that substantially inhibit emulsification of mineral fuel oils and lubricating oils.

The aforesaid metal salts of such citramic acids can be prepared by heating the citramic acids with the appropriate group II metals alkoxides, or metal hydroxides or, if desired, by use of an alkali metal hydroxide and double displacement with, for example, a group II metal halide (e.g., zinc chloride). Thus, for preparation of a normal metal salt (i.e., aforesaid Formulas A), one mole of the desired group II metal compound (e.g., alkoxide, hydroxide) is heated with two moles of the citramic acid; for preparation of the alkoxy metal salts (i.e., Formula B), one mole of the citramic acid is heated with one mole of the desired group II metal alkoxide; for preparation of the metal salts of Formulas C, one mole of the metal alkoxide or metal hydroxide with two moles of the monoamide of citric acid; and for Formulas D, two moles of the metal alkoxides or hydroxides with one mole of monoamide of citric acid.

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 substantially 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 D396–48T. Specifications for Diesel fuels are defined in ASTM Specifications D975–48T. Typical jet fuels are defined in Military Specification MIL–F–5624B.

The amount of the salt of citramic acid 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 and about 200 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 citramic acid 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 additive 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 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 citramic acid salts and 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 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 relatively 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, other amines as high as tertiary-triacontyl primary amine.

EXAMPLE 1

A mixture of 105 gms. (0.5 mole) of citric acid monohydrate, 200 gms. (1 mole) of Primene 81R and 300 cc. of xylene was refluxed at 145–150° C. for six hours to form the Primene 81R citramic acid. Water collected during the reflux was 27 cc. The Primene 81R citramic 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 150° C. and was held at 150° C. for one hour. The reaction product was distilled at 150° C. under house vacuum to remove all the xylene. The reac-

tion product which weighed 272 gms., theory 284 gms., was diluted with 272 gms. of a diluent (a paraffinic oil of 100 sec. at 100° F.) and filtered through Hyflo clay. The final product, the magnesium salt of Primene 81R citramic acid, which contained 50% diluent oil, was clear and fluid at room temperature.

Analysis, percent	Estimated	Found
Mg	1.1	1.09
N	2.5	2.52

EXAMPLE 2

A mixture of 105 gms. (0.5 mole) of citric acid monohydrate, 200 gms. (1 mole) of Primene 81R and 150 cc. of toluene was gradually heated to 150° C. and was held at 150° C. for 5 hours to insure the complete formation of the Primene 81R citramic acid. To the Primene 81R citramic acid was added at room temperature with stirring 79 gms. (0.25 mole) of barium hydroxide octahydrate and 312 gms. of diluent oil. The mixture was gradually heated to 150° C. and was held at 150° C. until the evolution of water ceased (about 2 hours). The reaction product was filtered through Hyflo clay. The final product, the barium salt of Primene 81R citramic acid, which contained 50% diluent oil, was clear and fluid at room temperature.

Analysis, percent	Estimated	Found
Ba	5.4	5.87
N	2.2	2.19

EXAMPLE 3

A mixture of 70 gms. (⅓ mole) of citric acid monohydrate, 133.4 gms. (⅔ mole) of Primene 81R and 200 cc. of toluene was refluxed at 125–135° C. for 3 hours and 150–155° C. for 3 hours to form the Primene 81R citramic acid. The amount of water collected during the reflux was 18 cc., theory 18 cc. To the Primene 81R citramic acid was added at room temperature with stirring 7.67 gms. (⅓ mole) of sodium in the form of a sodium methylate solution. The mixture was gradually heated to 150° C. and was held at 150° C. for one hour to insure the complete formation of the sodium salt. The sodium salt was diluted with 185 gms. of diluent oil and 100 cc. of benzene. To the sodium salt was added at room temperature with stirring 23 gms. (⅙ mole+4.5 gms. excess) of calcium chloride dissolved in 150 cc. of methanol. The mixture was gradually heated to 150° C. and was held at 150° C. for 2 hours. The reaction product was filtered through Hyflo clay easily. The final product, the calcium salt of the Primene 81R citramic acid, which contained 50% diluent oil was clear and fluid at room temperature.

Analysis, percent	Estimated	Found
Ca	1.75	2.12
N	2.5	2.39

EXAMPLE 4

A mixture of 70 gms. (⅓ mole) of citric acid monohydrate, 133.3 gms. (⅔ mole) of Primene 81R and 200 cc. of toluene was refluxed at 125–135° C. for 4 hours and 145–150° C. for 3 hours to form the Primene 81R citramic acid. The amount of water collected during the reflux was 19 cc., theory 18 cc. To the Primene 81R citramic acid was added at room temperature with stirring 7.67 gms. (⅓ mole) of sodium in the form of a sodium methylate solution. The mixture was gradually heated to 150° C. and was held at 150° C. for one hour to insure the complete formation of the sodium salt. The

sodium salt was diluted with 195 gms. of diluent oil and 100 cc. of benzene. To the sodium salt was added at room temperature with stirring 28.4 gms. (⅙ mole+5.7 gms. excess) of zinc chloride dissolved in 150 cc. of methanol. The mixture was gradually heated to 150° C. and was held at 150° C. for two hours. The reaction product was filtered through Hyflo clay. The final product, the zinc salt of the Primene 81R citramic acid, which contained 50% diluent oil, was clear and fluid at room temperature.

Analysis, percent	Estimated	Found
Zn	2.5	3.43
N	2.4	2.34

EXAMPLE 5

A mixture of 70 gms. (⅓ mole) of citric acid monohydrate, 133.3 gms. (⅔ mole) of Primene 81R and 200 cc. of toluene was refluxed at 115–125° C. for 3 hours and at 150–159° C. for 3 hours to form the Primene 81R citramic acid. Water collected during the reflux was 19 cc., theory 18 cc. The citramic acid, diluted with 370 gms. of diluent oil, was then added at room temperature with stirring to 8.1 gms. (⅓ mole) of magnesium in the form of a magnesium methylate solution. The mixture was gradually heated to 150° C. and then filtered through Hyflo clay. The final product, the methoxy magnesium salt of Primene 81R citramic acid, which contained 66⅔% diluent oil, was clear and fluid.

Analysis, percent	Estimated	Found
Mg	1.5	1.46
N	1.7	1.68

EXAMPLE 6

A mixture of 70 gms. (⅓ mole) of citric acid monohydrate, 133.3 gms. (⅔ mole) of Primene 81R and 200 cc. of toluene was refluxed at 115–125° C. for 2 hours and at 135–155° C. for 4 hours to form the Primene 81R citramic acid. Water collected during the reflux was 19 cc., theory 18 cc. The Primene 81R citramic acid, diluted with 412 gms. of diluent oil, was then added at room temperature with stirring to a zinc methylate solution obtained by refluxing 15.3 gms. (⅔ mole) of sodium in the form of a sodium methylate solution and 56.7 gms. (⅓ mole+11.4 gms. excess) of zinc chloride previously dissolved in 200 cc. of methanol. The mixture was gradually heated to 150° C. and was held at 150° C. for one hour. The reaction product was then filtered through Hyflo clay. The final product, the methoxy zinc salt of Primene 81R citramic acid, which contained 66⅔% diluent oil, was clear and fluid at room temperature.

Analysis, percent	Estimated	Found
Zn	3.5	3.98
N	1.5	1.47

EXAMPLE 7

A mixture of 105 gms. (0.5 mole) of citric acid monohydrate, 300 gms. (1 mole) of Primene JMT and 300 cc. of xylene was refluxed at 145–150° C. for 6 hours to form the Primene JMT citramic acid. Water collected was 27 cc., theory 27 cc. The Primene JMT citramic acid, diluted with 394 gms. of diluent oil, was then added at room temperature with stirring to 6.08 gms. (0.25 mole) of magnesium in the form of magnesium methylate solution. The mixture was gradually heated to 150° C. and was held at 150° C. for one hour. The reaction product was filtered through Hyflo clay and distilled to

150° C. under house vacuum to remove the xylene. The final product, the magnesium salt of Primene JMT citramic acid, which contained 50% diluent oil, was clear and fluid.

Analysis, percent	Estimated	Found
Mg	0.77	0.8
N	1.7	1.73

EXAMPLE 8

A mixture of 105 gms. (0.5 mole) of citric acid monohydrate, 300 gms. (1 mole) of Primene JMT and 150 cc. of toluene was refluxed at 125–135° C. for 3 hours and at 150–160° C. for 2 hours to form the Primene JMT citramic acid. Water collected during the reflux was 27 cc., theory 27 cc. To the Primene JMT citramic acid was added at room temperature with stirring 79 gms. (0.25 mole) of barium hydroxide octahydrate and 412 gms. of diluent oil. The mixture was gradually heated to 150° C. and was held at 150° C. for 2 hours. The reaction product was filtered through Hyflo clay. The final product, the barium salt of Primene JMT citramic acid, which contained 50% diluent oil, was clear and fluid at room temperature.

Analysis, percent	Estimated	Found
Ba	4.1	4.32
N	1.7	1.61

EXAMPLE 9

A mixture of 52.5 gms. (0.25 mole) of citric acid monohydrate, 150 gms. (0.5 mole) of Primene JMT and 200 cc. of toluene was refluxed at 117–135° C. for 2 hours and at 150–157° C. for 3 hours to form the Primene JMT citramic acid. The amount of water collected during the reflux was 14 cc., theory 13.5 cc. The Primene JMT citramic acid, diluted with 196 gms. of diluent oil, 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 150° C. and was held at 150° C. for one hour. The reaction product was filtered through Hyflo clay. The final product, the methoxy magnesium salt of Primene JMT citramic acid, which contained 50% diluent oil, was clear and fluid at room temperature.

Analysis, percent	Estimated	Found
Mg	1.5	1.46
N	1.7	1.68

EXAMPLE 10

A mixture of 70 gms. (⅓ mole) of citric acid monohydrate, 200 gms. (⅔ mole) of Primene JMT and 200 cc. of toluene was refluxed at 115–135° C. for 3 hours and at 145–155° C. for 3 hours to form the Primene JMT citramic acid. Water collected during the reflux was 19 cc., theory 18 cc. The Primene JMT citramic acid, diluted with 273 gms. of diluent oil, was then added at room temperature with stirring to a zinc methylate solution obtained by refluxing 15.3 gms. (⅔ mole) of sodium in the form of a sodium methylate solution and 56.7 gms. (⅓ mole+11.4 gms. excess) of zinc chloride previously dissolved in 200 cc. of methanol. The mixture was gradually heated to 150° C. and was held at 150° C. for one hour. The reaction product was filtered through Hyflo clay. The final product, the methoxy zinc salt of Primene JMT citramic acid, which contained 50% diluent oil, was clear and fluid at room temperature.

Analysis, percent	Estimated	Found
Zn	3.9	4.36
N	1.7	1.49

EXAMPLE 11

A mixture of 105 gms. (0.5 mole) of citric acid monohydrate, 100 gms. (0.5 mole) of Primene 81R and 184 gms. of xylene was refluxed at 135–142° C. until water stopped coming over (about 3 hours) to form the mono-Primene 81R citramic acid. To the mono-Primene 81R citramic acid was added at room temperature with stirring 6.08 gms. (0.25 mole) of magnesium in the form of a magnesium methylate solution. The mixture was gradually heated to 140° C. and was held there for one hour. The reaction product was filtered through Hyflo clay. The final product, the magnesium salt of mono-Primene 81R citramic acid, which contained approximately 50% xylene, was fluid at room temperature.

Analysis, percent	Estimated	Found
Mg	1.65	1.7
N	1.9	2.03

EXAMPLE 12

A mixture of 105 gms. (0.5 mole) of citric acid monohydrate, 150 gms. (0.5 mole) of Primene JMT and 200 cc. of xylene was refluxed at 135–145° C. until water stopped coming over (about 3 hours) to form the mono-Primene JMT citramic acid. To the mono-Primene JMT citramic acid was added at room temperature with stirring 6.08 gms. (0.25 mole) of magnesium in the form of a magnesium methylate solution. The mixture was gradually heated to 140° C. and was held there for 1 hour. The reaction product, diluted with 234 gms. of diluent oil, was filtered through Hyflo clay and distilled to 150° C. under house vacuum to remove all the xylene. The final product, the magnesium salt of mono-Primene JMT citramic acid, which contained approximately 50% diluent oil was fluid at room temperature.

Analysis, percent	Estimated	Found
Mg	1.28	1.45
N	1.49	1.58

EXAMPLE 13

A mixture of 105 gms. (0.5 mole) of citric acid monohydrate, 100 gms. (0.5 mole) of Primene 81R and 221 gms. of xylene was heated under reflux until water stopped coming over (about 3 hours) to form the mono-Primene 81R citramic acid. To the mono-Primene 81R citramic acid was added at room temperature with stirring 34.35 gms. (0.25 mole) of barium in the form of a barium methylate solution. The mixture was gradually heated to 125° C. and was held at 135° C. for one hour. The reaction product was filtered through Hyflo clay. The final product, the barium salt of mono-Primene 81R citramic acid, which contained approximately 50% xylene, was fluid at room temperature.

Analysis, percent	Estimated	Found
Ba	7.8	9.52
N	1.58	2.01

EXAMPLE 14

A mixture of 105 gms. (0.5 mole) of citric acid monohydrate, 150 gms. (0.5 mole) of Primene JMT and 200 cc. of xylene was refluxed at 135–145° C. until water stopped coming over (about 3 hours) to form the

mono-Primene JMT citramic acid. To the mono-Primene JMT citramic acid was added at room temperature with stirring 34.35 gms. (0.25 mole) of barium in the form of a barium methylate solution and 271 gms. of diluent oil. The mixture was gradually heated to 155° C. and was held at 155° C. until the xylene stopped coming over. The reaction product was filtered through Hyflo clay. The final product, the barium salt of mono-Primene JMT citramic acid, which contained approximately 50% diluent oil, was fluid at room temperature.

Analysis, percent	Estimated	Found
Ba	6.3	6.64
N	1.29	1.36

EXAMPLE 15

A mixture of 105 gms. (0.5 mole) of citric acid monohydrate, 150 gms. (0.5 mole) of Primene JMT and 200 cc. of xylene was refluxed at 135–145° C. until water stopped coming over (about 3 hours) to form the mono-Primene JMT citramic acid. To the mono-Primene JMT citramic acid was added at room temperature with stirring 11.5 gms. (0.5 mole) of sodium in the form of a sodium methylate solution. The mixture was gradually heated to 135° C. to form the sodium salt. To the sodium salt was added at room temperature with stirring 42 gms. (0.25 mole+8 gms. excess) of $ZnCl_2$ dissolved in 200 cc. of methanol. The mixture was gradually heated to 150° C. and was held at 150° C. for 2 hours. The reaction product was diluted with 242 gms. of diluent oil and filtered through Hyflo clay. The final product, the zinc salt of mono-Primene JMT citramic acid, which contained approximately 50% diluent oil was fluid at room temperature.

Analysis, percent	Estimated	Found
Zn	3.3	4.24
N	1.45	1.53

EXAMPLE 16

A mixture of 105 gms. (0.5 mole) of citric acid monohydrate, 100 gms. (0.5 mole) of Primene 81R and 200 gms. of xylene was refluxed at 135–142° C. until water stopped coming over to form the mono-Primene 81R citramic acid. To the mono-Primene 81R citramic acid was added at room temperature with stirring 11.5 gms. (0.5 mole) of sodium in the form of a sodium methylate solution. The mixture was gradually heated to 135° C. to form the sodium salt. To the sodium salt was added at room temperature with stirring 42 gms. (0.25 mole+8 gms. excess) of $ZnCl_2$ dissolved in 200 cc. of methanol. The mixture was gradually heated to 135° C. The reaction product was filtered through Hyflo clay. The final product, the zinc salt of mono-Primene 81R citramic acid, which contains approximately 50% xylene, was fluid at room temperature.

Analysis, percent	Estimated	Found
Zn	4.2	5.24
N	1.8	1.97

EXAMPLE 17

A mixture of 105 gms. (0.5 mole) of citric acid monohydrate, 150 gms. (0.5 mole) of Primene JMT and 200 cc. xylene was refluxed at 135–145° C. until water stopped coming over (about 3 hours) to form the mono-Primene JMT citramic acid. To the mono-Primene JMT citramic acid was added at room temperature with stirring 11.5 gms. (0.5 mole) of Na in the form of a sodium methylate solution. The mixture was gradually heated to 135° C. to form the sodium salt. The sodium salt was diluted with 247 gms. of diluent oil. To the sodium salt was added at room temperature with stirring 34.8 gms. (0.25 mole+7 gms. excess) of $CaCl_2$ dissolved in 200 cc. of methanol. The mixture was gradually heated to 150° C. and was held at 150–155° C. for one hour. The reaction product was filtered through Hyflo clay. The final product, the calcium salt of mono-Primene JMT citramic acid, which contained approximately 50% diluent oil, was fluid at room temperature.

Analysis, percent	Estimated	Found
Ca	2.0	2.93
N	1.4	1.86

EXAMPLE 18

A mixture of 105 gms. (0.5 mole) of citric acid monohydrate, 100 gms. (0.5 mole) of Primene 81R and 187 gms. of xylene was refluxed at 135–142° C. until water stopped coming over (about 3 hours) to form the mono-Primene 81R citramic acid. To the mono-Primene 81R citramic acid was added at room temperature with stirring 11.5 gms. (0.5 mole) of sodium in the form of a sodium methylate solution. The mixture was gradually heated to 135° C. to form the sodium salt. To the sodium salt was added at room temperature with stirring 34.8 gms. (0.25 mole+7 gms. excess) of $CaCl_2$ dissolved in 300 cc. of methanol. The mixture was gradually heated to 125° C. and was held at 125° C. for one hour. The reaction product was filtered through Hyflo clay steadily. The final product, which contained approximately 50% xylene, was fluid at room temperature.

Analysis, percent	Estimated	Found
Ca	2.8	2.64
N	1.9	1.53

EXAMPLE 19

A mixture of 105 gms. (0.5 mole) of citric acid monohydrate, 150 gms. (0.5 mole) of Armeen S and 250 gms. of xylene was refluxed at 135–142° C. to form the mono-Armeen S citramic acid. To the mono-Armeen S citramic acid was added at room temperature with stirring 6.08 gms. (0.25 mole) of magnesium in the form of a magnesium methylate solution. The mixture was gradually heated to 130° C. The reaction product, being viscous, was diluted with 234 gms. of xylene and filtered through Hyflo clay. The final product, the magnesium salt of mono-Armeen S citramic acid, which contained approximately 66⅔% xylene was fluid at room temperature.

Analysis, percent	Estimated	Found
Mg	0.87	0.83
N	1.00	1.00

EXAMPLE 20

A mixture of 52.5 gms. (0.25 mole) of citric acid monohydrate, 150 gms. (0.5 mole) of Armeen S, and 400 cc. of xylene was refluxed at 140° C. for about 5 hours to form the di-Armeen S citramic acid. To the di-Armeen S citramic acid was added at room temperature with stirring 3.04 gms. (0.125 mole) of magnesium in the form of a magnesium methylate solution and 191 gms. of diluent oil. The mixture was gradually heated to 155° C. and was held there for one hour. The reaction product was filtered through Hyflo clay. The final product, the magnesium salt of di-Armeen S citramic acid, which contained 50% diluent oil, was fluid at room temperature.

Analysis, percent	Estimated	Found
Mg	0.78	0.61
N	1.9	1.93

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. This 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 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	Concn. lb./1,000 bbls.	Screen clogging, percent
Uninhibited fuel blend	0	100
Uninhibited fuel blend+Ex. 1	50	7
Uninhibited fuel blend+Ex. 2	50	9
Uninhibited fuel blend+Ex. 3	50	15
Uninhibited fuel blend+Ex. 4	50	7
Uninhibited fuel blend+Ex. 5	50	7
Uninhibited fuel blend+Ex. 6	50	8
Uninhibited fuel blend+Ex. 7	25	10
Uninhibited fuel blend+Ex. 8	50	10
Uninhibited fuel blend+Ex. 9	50	7
Uninhibited fuel blend+Ex. 10	50	15
Uninhibited fuel blend+Ex. 11	25	2
Uninhibited fuel blend+Ex. 12	50	2
Uninhibited fuel blend+Ex. 13	50	2
Uninhibited fuel blend+Ex. 14	50	4
Uninhibited fuel blend+Ex. 15	25	9
Uninhibited fuel blend+Ex. 16	50	4
Uninhibited fuel blend+Ex. 17	25	4
Uninhibited fuel blend+Ex. 18	50	5

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 convected 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 inhibited 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	21
Uninhibited fuel blend+Ex. 1	25	5
Uninhibited fuel blend	0	18
Uninhibited fuel blend+Ex. 2	25	15
Uninhibited fuel blend	0	76
Uninhibited fuel blend+Ex. 3	50	27
Uninhibited fuel blend	0	77
Uninhibited fuel blend+Ex. 4	50	61
Uninhibited fuel blend	0	77
Uninhibited fuel blend+Ex. 5	50	17
Uninhibited fuel blend	0	77
Uninhibited fuel blend+Ex. 7	50	36
Uninhibited fuel blend	0	18
Uninhibited fuel blend+Ex. 8	25	3
Uninhibited fuel blend	0	77
Uninhibited fuel blend+Ex. 9	50	25
Uninhibited fuel blend	0	129
Uninhibited fuel blend+Ex. 11	50	56
Uninhibited fuel blend	0	20
Uninhibited fuel blend+Ex. 12	25	2
Uninhibited fuel blend	0	20
Uninhibited fuel blend+Ex. 13	25	3
Uninhibited fuel blend	0	129
Uninhibited fuel blend+Ex. 14	50	41
Uninhibited fuel blend	0	129
Uninhibited fuel blend+Ex. 17	25	70
Uninhibited fuel blend	0	129
Uninhibited fuel blend+Ex. 18	25	57

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 anti-rust 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+Ex. 1	10	Pass.
Blank fuel blend+Ex. 2	10	Do.
Blank fuel blend+Ex. 3	10	Do.
Blank fuel blend+Ex. 4	50	Do.
Blank fuel blend+Ex. 5	10	Do.
Blank fuel blend+Ex. 7	10	Do.
Blank fuel blend+Ex. 8	10	Do.
Blank fuel blend+Ex. 9	10	Do.
Blank fuel blend+Ex. 10	50	Do.
Blank fuel blend+Ex. 11	10	Do.
Blank fuel blend+Ex. 12	10	Do.
Blank fuel blend+Ex. 13	10	Do.
Blank fuel blend+Ex. 14	10	Do.
Blank fuel blend+Ex. 15	10	Do.
Blank fuel blend+Ex. 16	10	Do.
Blank fuel blend+Ex. 17	10	Do.
Blank fuel blend+Ex. 18	50	Do.

TABLE IV

TABLE IV.—ASTM RUST TEST D-665

[Inhibitors blended in a light turbine oil]

	Concn. wt. percent	Rust test result
Blank light turbine oil	0	Fail.
Blank light turbine oil+Ex. 1	0.2	Pass.
Blank light turbine oil+Ex. 2	0.2	Do.
Blank light turbine oil+Ex. 3	0.2	Do.
Blank light turbine oil+Ex. 4	0.3	Do.
Blank light turbine oil+Ex. 6	0.2	Do.
Blank light turbine oil+Ex. 7	0.2	Do.
Blank light turbine oil+Ex. 9	0.4	Do.
Blank light turbine oil+Ex. 12	0.2	Do.
Blank light turbine oil+Ex. 14	0.2	Do.
Blank light turbine oil+Ex. 15	0.2	Do.
Blank light turbine oil+Ex. 17	0.2	Do.

As is apparent from the data in Tables III and IV, the addition agents of this invention effectively inhibited the fuel oils and turbine 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 amide 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 aliphatic group, such salts induce severe emulsification with water. In example, reference is made to Examples 19 and 20 showing preparation of a magnesium salt of a citramic acid derived from a normal amine (Armeen S)which is a mixture of primary amines comprised of approximately 10% hexadecylamine, 10% octadecylamine, 35% octadecenylamine and 45% octadecadienyl. 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 11 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 19 and such fuel oil compositions were subjected to the following emulsion test:

Emulsion test

The procedure for the fuel oil emulsion test 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 hour 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 is 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

Rating	Description of emulsion
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:

	Concn. of additive lbs./1,000 bbls.	Rating
Base Fuel + Ex. 11	25	2
Base Fuel + Ex. 19	25	9

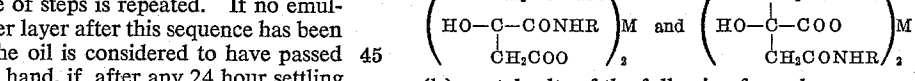
It is apparent from the foregoing that the magnesium salt of mono-Primene 81R citramic acid (Ex. 11) containing a tertiary carbon atom attached to the nitrogen atom effectively inhibited emulsification (Rating 2) whereas the corresponding magnesium salt (Ex. 19) but prepared from the normal amine (Armeen S) resulted in a composition that emulsified severely (Rating 9).

Although the present invention has been described with preferred embodiments, it is to be understood that modifications and variations may be resorted to, without departing from the spirit and scope of this invention, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the appended claims.

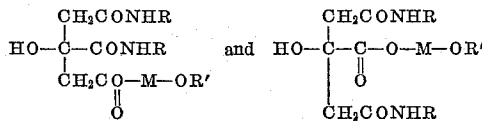
What is claimed is:

1. As a new composition, a liquid mineral oil containing from about one to about 200 pounds per thousand barrels of said oil of a compound from the group consisting of:

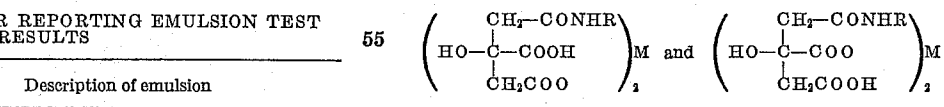
(a) metal salts of the following formulas:



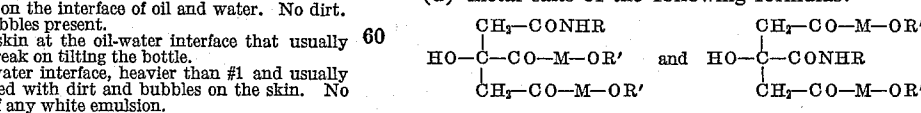
(b) metal salts of the following formulas:



(c) metal salts of the following formulas:



(d) metal salts of the following formulas:



and mixtures thereof, wherein M is a Group II metal, R is an alkyl group of from four to about thirty carbon atoms and has a tertiary carbon atom attached to the nitrogen atom, and R' is a saturated aliphatic hydrocarbon group.

2. A composition, as defined in claim **1**, wherein the mineral oil is 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 R' is a saturated aliphatic hydrocarbon group of from one to eighteen carbon atoms.

5. A composition, as defined in claim 1, wherein M is a metal from the group consisting of magnesium, barium, calcium, and zinc.

6. A composition, as defined in claim 1, wherein R contains 12 to 24 carbon atoms.

7. A composition, as defined in claim 1, wherein R contains 12 to 24 carbon atoms, R' contains one to eighteen carbon atoms and M is a metal from the group consisting of magnesium, barium, calcium and zinc.

8. A composition, as defined in claim 7, 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.

9. A composition, as defined in claim 7, wherein the mineral oil is a lubricating oil.

10. A composition, as defined in claim 7, wherein R' is a methyl group.

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