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FUEL OIL AND LUBRICATING OIL COMPOSITIONS CONTAINING METAL SALTS OF THE MONO-AMIDES OF TETRAPROPENYL SUCCINIC ACID

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The present invention relates to improved fuel oil compositions and improved lubricating oil compositions, each containing metal salts of certain mono-amides of tetrapropenyl succinic acid. More particularly, the invention is concerned with both fuel compositions and lubricating compositions containing metal salts of certain mono-amides of tetrapropenyl succinic acid, which metal salts impart improved anti-screen clogging, sediment stabilization, and anti-rust characteristics to the fuels, and the combination of anti-rust and anti-tin-babbitt corrosion as well as good demulsibility qualities to the lubricating oils.

It is well known that fuel oil compositions are prone to form sludge or sediment during periods of prolonged storage. This sediment has, of course, many adverse effects such as on burner operation due to its tendency to clog screens and nozzles. In addition, other impurities such as rust, dirt and entrained water, which are often present in fuels, tend to settle out and thereby clog various equipment parts such as nozzles, screens, filters, etc. Furthermore, while in storage tanks, fuel oils tend to accumulate considerable amounts of water. This water creates a rust problem both in the storage tank and during the transportation of the fuels in pipelines, tankers and the like.

In the field of lubrication, the rusting of ferrous metal surfaces and the corrosion of tin-babbitt (alloys of tin, copper and antimony) surfaces is a well recognized problem. This is often a serious problem in steam turbine engines, particularly marine turbines which are exposed to the rusting and corrosive action of sea water. The formation of rust and corrosion in the engines is also often caused by water entering the oil supply as by condensation, and thereafter circulating throughout the oil system to contact the ferrous and tin-babbitt metal surfaces. The tendency of lubricating oils to form emulsions, i.e., intimate mixtures of oil and water, is also a prevalent lubricating problem since these emulsions promote the collection of dirt, grit, and foreign matter in the oil, which materials can cause abrasive wear on the parts to be lubricated. It is therefore desirable that lubricating oils possess good demulsibility characteristics, since if the emulsion breaks quickly, these harmful effects are reduced.

Generally, it has been the practice to overcome the aforedescribed fuel oil and lubricating oil problems by the use of a separate additive for each purpose, i.e., a sediment inhibitor, an anti-screen clogging agent, and an anti-rust agent in the fuel oils; and an anti-rust agent, anti-tin-babbitt corrosion agent and anti-emulsifying or demulsification agent in the lubricating compositions.

We have now found that by the use of a single additive it is possible to largely overcome the abovementioned difficulties. It will, of course, be appreciated that the use of a single additive for a variety of purposes is highly desirable both from the point of view of simplicity of operation and economy of materials.

We have found that the addition of metal salts of certain mono-amides of succinic acid to fuel oil and mineral oil compositions imparts anti-screen clogging characteristics, anti-rust properties and sediment stabilization or sediment formation-inhibiting characteristics to the fuel oils; while also imparting anti-rust, anti-tin-babbitt corrosion and demulsification properties to the lubricating compositions.

Accordingly, it is an object of the present invention to provide improved fuel oil and lubricating oil compositions possessing the abovementioned desirable properties.

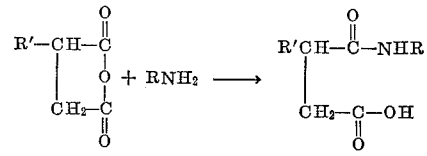
A further object is to provide a method for obtaining fuel oils exhibiting anti-screen clogging, anti-rust and sediment stabilization qualities and lubricating compositions possessing the combination of anti-rust and anti-tin-babbitt corrosion properties as well as good demulsibility characteristics.

Other objects of the invention and the advantages thereof will become hereinafter apparent.

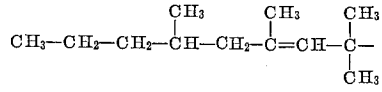
The additive agents of the present invention are metal salts of the mono-amides of tetrapropenyl succinic acid, wherein the amide groups are derived from tertiary-alkyl primary amines possessing a tertiary carbon atom attached to the primary amino ($-NH_2$) group.

In general, the metal salts may be prepared by reacting a t-alkyl-containing mono-amide of tetrapropenyl succinic acid with an hydroxide, alkoxide or oxide of the desired metal at elevated temperatures.

These intermediate mono-amides of tetrapropenyl succinic acid can be prepared by several methods such as, for example, by reacting at least about 1 mole of a tertiary-alkyl primary mono-amine containing a tertiary carbon atom attached to the amino group, with at least about 1 mole of tetrapropenyl succinic anhydride. The reaction may be conducted at any suitable temperature such as at room temperature or preferably at a temperature of from about 75–100° C. for from 1 to 3 hours. It is thought that this reaction occurs according to the following equation:



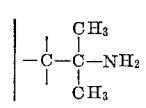
wherein R′ is a tetrapropenyl group having, for example, a structure such as:



and R represents the hydrocarbon portion of the tertiary-alkyl primary aliphatic amine.

In order to obtain the metal salts which are used in the compositions of the present invention, the resulting mono-amides are then heated with the metal alkoxide, hydroxide or oxide, at elevated temperatures, preferably at a temperature of from about 100 to about 175° C. to form the desired metal salts. The reaction time, which will, of course, depend on the particular temperature employed, is preferably from about 1 to about 5 hours.

The mono-amido components of the instant metal salts are obtained from tertiary-alkyl primary mono-amines wherein the amino group is attached to a tertiary carbon atom and which contain from about 4 to about 30 carbon atoms in the tertiary alkyl radical. These amines therefore all contain the terminal group,



Some non-limiting examples of suitable tertiary-alkyl primary amines are t-butyl, t-hexyl, t-nonyl, t-decyl, t-dodecyl, t-tetradecyl, t-octadecyl, t-eicosyl, t-docosyl, -tetracosyl, t-tricontyl, etc. primary amines or mixtures thereof. The preparation of these t-alkyl primary amines or mixtures thereof is known to the art and several suit-

able methods are available such as, for example, that described in the Journal of Organic Chemistry, volume 20, page 295 et seq. (1955).

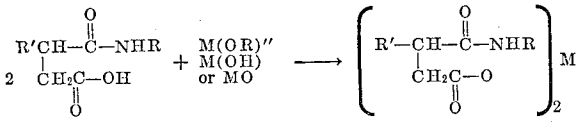
The metals used in the additives of the present invention may be selected from the metals of groups II and III of the Mendeleeff Periodic Table. The metals salts of the mono-amides of tetrapropenyl succinic acid wherein the metal is zinc, calcium, barium, magnesium and aluminum are particularly suitable.

The particular type of metal salt produced will depend on the relative proportions of the mono-amide and the metal compound and the particular nature thereof.

In general, the normal salts are prepared by heating together at least about two moles of the mono-amide of tetrapropenyl succinic acid per mole of metal compound, the alkoxy metal salts are produced using at least about one mole of mono-amide per mole of metal alkoxy, while the complex alkoxy metal salts are obtained when using about two or more moles of metal alkoxy per mole of mono-amide.

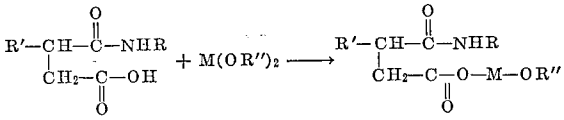
Although the present invention is not limited to any particular theory for the salt-forming reactions, it is thought that the formation of the metal salt takes place in the following manner.

Normal salts:

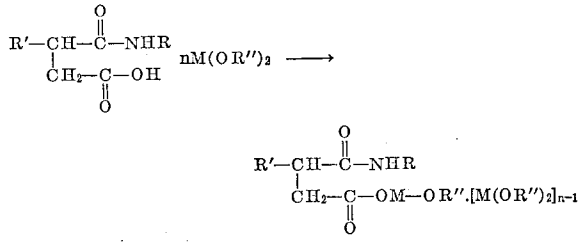


wherein M represents a group II or III metal, R and R' have the meanings given above, and R'' represents an alkyl group containing one or more carbon atoms.

Alkoxy metal salt:



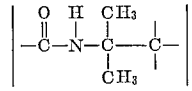
Complex alkoxy metal salt:



wherein *n* is at least 2.

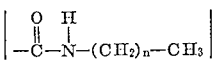
It should be noted that the term tetrapropenyl as used herein also encompasses mixtures of tertiary olefins containing 12–15 carbon atoms, averaging 12 carbon atoms, and containing predominant portions of C_{12} tertiary olefins. A typical tetrapropenyl mixture may contain, for example 85% of a tertiary C_{12} olefin, 10% of a tertiary C_{15} olefin along with relatively small amounts, i.e., less than about 5 percent of tertiary olefins having less than 12 or more than 15 carbon atoms.

It should be noted that it is critical that the mono-amido nitrogen atom of the additives of the present invention possesses a hydrogen atom and be attached to the tertiary carbon atom of the tertiary alkyl group, according to the following structure:

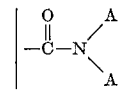


This of course, means that the amido component must be derived from a tertiary-alkyl primary amine containing a tertiary carbon attached to the nitrogen atom.

Indeed, the corresponding metal salts of tetrapropenyl succinamic acid wherein the amido group is derived from a normal primary amine as shown in the following structure:



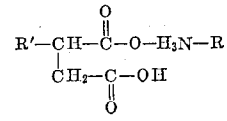
(*n* having a value, for example, from about 3 to 30); or wherein the amido group is derived from a secondary amine so that both hydrogen atoms of the amido nitrogen atom are substituted according to the following arrangement:



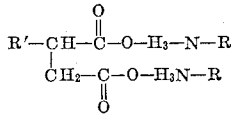
(A being a hydrocarbon or substituted hydrocarbon radical) do not exhibit the desirable combination of additive properties possessed by the metal salts of the present invention.

For example, upon the addition of the instant metal salts wherein the amido nitrogen is attached to the tertiary carbon of a tertiary-alkyl group, to lubricating oils such as turbine oils, the resulting oils are found to exhibit the unusual combination of both anti-rust and anti-tin-babbitt corrosion characteristics as well as good demulsibility. By contrast, upon substituting similar metal salts of tetrapropenyl succinic acid mono-amide, which contain, however, the amido nitrogen attached to a normal alkyl group, it is found that the resulting turbine oils fail to possess satisfactory demulsibility characteristics.

It is believed that the combination of both anti-rust and anti-tin-babbitt corrosion qualities which the instant metal salts impart to lubricating oils, is quite unexpected. This is particularly the case since, first of all, the corresponding amine salts of the instant tetrapropenyl succinic acids, that is, compounds having the formulas:



or



wherein R' and R are tetrapropenyl and tertiary-alkyl groups as described above, fail to impart anti-tin-babbitt corrosion qualities to lubricating oils. Secondly, it is known in the art that additives imparting anti-rust properties to oils are generally not capable of also inhibiting the tin-babbitt corrosion.

The metal salts of the mono-amides of tetrapropenyl succinamic acid of the present invention may be advantageously employed in a wide variety of fuel and lubricating compositions.

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 hereinabove, 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 specification 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 motor fuels contemplated herein are mixtures of hydrocarbons suitable for use in internal combustion engines of the spark-ignition type. These fuels include both motor gasolines and aviation gasolines. In general, motor gasolines have an initial boiling point as low as about 80° F. and an end-boiling point as high as about 440° F. and boils substantially continuously between the initial boiling point and the end-boiling point. Aviation gasolines, on the other hand, are mixtures of hydrocarbons having an initial boiling point of about 80° F. and an end-boiling point of about 340° F. and boiling substantially continuously between these points.

The instant metal salts may be used in any type of lubricating oil ranging from gasoline and kerosene to petrolatum or petroleum wax.

These metals salts are particularly adapted for use in turbine oils.

The particular amounts of tetrapropenyl succinamic acid metal salts employed will depend, of course, on the nature of the fuel or lubricating composition and their intended use. In general, the amount of additive that can be added to the oil will vary between about one pound per thousand barrels of fuel and about 200 pounds per thousand barrels of fuel. Preferably, it will vary between about 10 and about 200 pounds per thousand barrels of fuel.

In lube oils concentrations may range from 0.001% to 1.0%, the preferred range being 0.01% to 0.05% by weight.

The fuel and lubricating compositions of the present invention may, of course, also contain effective quantities of various other typical fuel and lubricant additives respectively including fuel additives such as foam inhibitors, ignition or burning quality improvers; lubricant additives such as detergents, anti-oxidants, V.I. improvers, etc.

The following specific examples are given in order to illustrate the present invention. It should be understood, however, that the invention is not limited to the particular additives, fuels, lubricants or manipulations described therein.

The particular tertiary-alkyl primary amines used in the working examples are mixtures of pure amines. "Amine A" is a mixture of primary amines having a carbon atom of a tertiary butyl group attached to the amino (—NH_2) group and containing 12 to 15 carbon atoms per amine molecule and averaging about 12 carbon atoms per molecule. This mixture contains, by weight, about 85 percent tertiary dodecyl amine, about 10 percent tertiary pentadecyl amine, and relatively small amounts, i.e., less than about 5 percent of amines having less than 12 or more than 15 carbon atoms. "Amine B" is a similar type of tertiary-alkyl primary amine mixture with the number of carbon atoms therein varying from 18 to 24 per amine molecule.

In addition, "Amine A" and "Amine B" possess the following characteristics:

	"Amine A"	"Amine B"
Molecular Weight	Principally 185–227.	Principally 269–353.
Boiling Range (760 mm.)	5–90% at 223–240° C.	5–70% at 232–315° C.
Specific Gravity, 25° C	0.812	0.845.
Flash point (Tag., open cup)	205° F	260° F.

EXAMPLE 1

A mixture of 133 gms. (0.5 mole) of tetrapropenyl succinic anhydride, 100 gms. (0.5 mole) of "Amine A" and 100 cc. of toluene as a diluent was stirred at 95° C. for 2 hours to form the corresponding mono-amide of tetrapropenyl succinic acid. To this tetrapropenyl succinic acid mono-amide, 6 gms. (0.25 mole) of Mg in the form of a magnesium methylate solution and 240 gms. of paraffinic oil (a conventionally refined paraffin oil having a viscosity of 128–138 S.U.V. at 100° F.) was added at room temperature with stirring. The mixture was gradually heated to 175° C. and was held at 175° C. for one hour. The reaction product was filtered through "Hyflo" clay (a diatomaceous earth filter aide) easily. The final product, the magnesium salt of tetrapropenyl succinic acid monoamide, which contained 50 percent paraffinic oil, was clear and fluid at the room temperature and analyzed as follows:

Analysis	Estimated	Found
Percent Mg	1.25	1.28
Percent N	1.46	1.50

EXAMPLE 2

A mixture of 133 gms. (0.5 mole) of tetrapropenyl succinic anhydride, 150 gms. (0.5 mole) of "Amine B" and 100 cc. of toluene as a diluent was stirred at 95° C. for two hours to form the corresponding mono-amide of tetrapropenyl succinic acid. To this tetrapropenyl succinic acid mono-amide, 6 gms. (0.25 mole) of Mg in the form of a magnesium methylate solution and 290 gms. of paraffinic oil was added at room temperature with stirring. The mixture was gradually heated to 175° C. and was held at 175° C. for one hour. The reaction product was filtered through "Hyflo" clay easily. The final product, the magnesium salt of tetrapropenyl succinic acid mono-amide, which contained 50 percent paraffinic oil was clear and fluid at room temperature and gave the following analysis:

Analysis	Estimated	Found
Percent Mg	1.03	1.05
Percent N	1.2	1.19

EXAMPLE 3

A mixture of 133 gms. (0.5 mole) of tetrapropenyl succinic anhydride, 100 gms. (0.5 mole) of "Amine A" and 100 cc. of toluene was heated with stirring at 95° C. for two hours to form the corresponding mono-amide of tetrapropenyl succinic acid. To this tetrapropenyl succinic acid mono-amide, 250 gms. of paraffinic oil, 44 gms. (0.25 mole+10 gms. excess) of $ZnCl_2$ dissolved in 200 cc. of methanol and 20 gms. (0.5 mole) of NaOH dissolved in 200 cc. of methanol was added at room temperature. The mixture was gradually heated to 175° C. and was held at 175° C. for two hours. The reaction product was filtered through "Hyflo" clay easily. The final product, the zinc salt of tetrapropenyl succinic acid mono-amide, which contained 50 percent paraffinic oil

was clear and fluid at room temperature and gave the following analytical results:

Analysis	Estimated	Found
Percent Zn	3.2	3.37
Percent N	1.4	1.38

EXAMPLE 4

A mixture of 133 gms. (0.5 mole) of tetrapropenyl succinic anhydride, 150 gms. (0.5 mole) of "Amine B" and 100 cc. of xylene was stirred at 95° C. for two hours to form the corresponding mono-amide of tetrapropenyl succinic acid. To this tetrapropenyl succinic acid mono-amide, 20 gms. (0.5 mole) of NaOH dissolved in 200 cc. of methanol was added at room temperature with stirring. The mixture was gradually heated to 175° C. to form the sodum salt of the mono-amide tetrapropenyl succinic acid. The sodium salt of the mono-amide tetrapropenyl succinic acid was diluted with 100 cc. of toluene and 299 gms. of paraffinic oil. To the sodium salt was added at room temperature 44 gms. (0.25 mole+10 gms. excess) of $ZnCl_2$ dissolved in 200 cc. of methanol. The mixture was gradually heated to 175° C. and was held at 175° C. for two hours. The reaction product was filtered through "Hyflo" clay easily. The final product, the zinc salt of tetrapropenyl succinic acid mono-amide, which contained 50 percent paraffinic oil was clear and fluid at room temperature and gave the following analytical results:

Analysis	Estimated	Found
Percent Zn	2.7	3.36
Percent N	1.1	1.07

EXAMPLE 5

A mixture of 133 gms. (0.5 mole) of tetrapropenyl succinic anhydride, 100 gms. (0.5 mole) of "Amine A" and 100 cc. of toluene was stirred at 95° C. for two hours to form the corresponding mono-amide of tetrapropenyl succinic acid. To this tetrapropenyl succinic acid mono-amide, 18.5 gms. (0.25 mole) of $Ca(OH)_2$ and 244 gms. of paraffinic oil was added at room temperature with stirring. The mixture was gradually heated to 175° C. and was held at 175° C. for one hour. The reaction product was filtered through "Hyflo" clay easily. The final product, the calcium salt of tetrapropenyl succinic acid mono-amide, which contained 50 percent paraffinic oil, was clear and fluid at room temperature and gave the following analytical results:

Analysis	Estimated	Found
Percent Ca	2.05	2.01
Percent N	1.45	1.44

EXAMPLE 6

A mixture of 133 gms. (0.5 mole) of tetrapropenyl succinic anhydride, 100 gms. (0.5 mole) of "Amine B" and 100 cc. of xylene was stirred at 95° C. for two hours to form the corresponding mono-amide tetrapropenyl succinic acid. To this tetrapropenyl succinic acid mono-amide, 18.5 gms. (0.25 mole) of $Ca(OH)_2$ and 293 gms. of paraffinic oil was added at room temperature with stirring. The mixture was gradually heated to 175° C. and was held at 175° C. for one hour. The reaction product was filtered through "Hyflo" clay easily. The final product, the calcium salt of the mono-amide of tetrapropenyl succinic acid was clear and fluid at room temperature and gave the following analytical results:

Analysis	Estimated	Found
Percent Ca	1.7	1.71
Percent N	1.2	1.31

EXAMPLE 7

A mixture of 133 gms. (0.5 mole) of tetrapropenyl succinic anhydride, 100 gms. (0.5 mole) of "Amine A" and 100 cc. of xylene was stirred at 95° C. for two hours to form the corresponding mono-amide of tetrapropenyl succinic acid. To this tetrapropenyl succinic acid mono-amide, 78.75 gms. (0.25 mole) of barium hydroxide octahydrate and 267 gms. of paraffinic oil was added at room temperature with stirring. The mixture was gradually heated to 175° C. and was held at 175° C. for two hours. The reaction product was filtered through "Hyflo" clay steadily. The final product, the barium salt of the mono-amide of tetrapropenyl succinic acid, which contained 50 percent paraffinic oil, was clear and fluid at room temperature and gave the following analytical results.

Analysis	Estimated	Found
Percent Ba	6.3	6.37
Percent N	1.3	1.31

EXAMPLE 8

A mixture of 133 gms. (0.5 mole) of tetrapropenyl succinic anhydride, 150 gms. (0.5 mole) of "Amine A" and 100 cc. of toluene was stirred at 95° C. for two hours to form the corresponding mono-amide of tetrapropenyl succinic acid. To this tetrapropenyl succinic acid mono-amide, 34.25 gms. (0.25 mole) of barium in the form of a barium methylate solution and 268 gms. of paraffinic oil was added at room temperature with stirring. The mixture was gradually heated to 175° C. and was held at 175° C. for one hour. The reaction mixture was filtered through "Hyflo" clay easily. The final product, the barium salt of the mono-amide of tetrapropenyl succinic acid, which contained 50 percent paraffinic oil was clear and fluid at room temperature and gave the following analytical results:

Analysis	Estimated	Found
Percent Ba	5.9	6.41
Percent N	1.2	1.25

EXAMPLE 9

A mixture of 133 gms. (0.5 mole) of tetrapropenyl succinic anhydride, 100 gms. (0.5 mole) of "Amine A" and 100 cc. of toluene was stirred at 95° C. for two hours to form the corresponding mono-amide of tetrapropenyl succinic acid. The tetrapropenyl succinic acid mono-amide, diluted with 237 gms. of paraffinic oil was then added at room temperature with stirring to 4.5 gms. (⅓ mole) of aluminum in the form of an aluminum butylate solution. The mixture was gradually heated to 175° C. and was held at 175° C. for one hour. The reaction product was filtered through "Hyflo" clay steadily. The final product, the aluminum salt of the mono-amide of tetrapropenyl succinic acid, which contained 50 percent paraffinic oil was

clear and fluid at room temperature and gave the following analytical results:

Analysis	Estimated	Found
Percent Al	0.97	0.98
Percent N	1.4	1.51

EXAMPLE 10

A mixture of 133 gms. (0.5 mole) of tetrapropenyl succinic anhydride, 100 gms. (0.5 mole) of "Amine A" and 75 cc. of benzene was heated with stirring at 95° C. for two hours to form the corresponding mono-amide of tetrapropenyl succinic acid. This tetrapropenyl succinic acid mono-amide, diluted with 245 gms. of paraffinic oil, was then added at room temperature with stirring to 12.16 gms. (0.5 mole) of Mg in the form of a magnesium methylate solution. The mixture was gradually heated to 125° C. with stirring and was held at 125° C. until all the methanol and benzene stopped coming over (about two hours). The reaction product was filtered through "Hyflo" clay easily. The final product, the methoxy magnesium salt of the mono-amide tetrapropenyl succinic acid, which contained 50 percent paraffinic oil, was clear and fluid at room temperature and gave the following results upon analysis:

Analysis	Estimated	Found
Percent Mg	2.4	2.44
Percent N	1.4	1.32

EXAMPLE 11

A mixture of 133 gms. (0.5 mole) of tetrapropenyl succinic anhydride, 150 gms. (0.5 mole) of "Amnie B" and 75 cc. of benzene was heated with stirring at 95° C. for two hours to form the corresponding mono-amide of tetrapropenyl succinic acid. The tetrapropenyl succinic acid mono-amide, diluted with 295 gms. of paraffinic oil was then added at room temperature with stirring to 12.16 gms. (0.5 mole) of magnesium in the form of a magnesium methylate solution. The mixture was gradually heated to 125° C. and was held at 125° C. until the methanol and benzene stopped coming over (about two hours). The reaction product was filtered through "Hyflo" clay. The final product, the methoxy magnesium salt of the mono-amide of tetrapropenyl succinic acid, which contained 50 percent paraffinic oil was clear and fluid at room temperature and gave the following results upon analysis:

Analysis	Estimated	Found
Percent Mg	2.0	2.1
Percent N	1.1	1.0

EXAMPLE 12

A mixture of 133 gms. (0.5 mole) of tetrapropenyl succinic anhydride, 100 gms. (0.5 mole) of "Amine A" and 100 cc. of benzene was heated with stirring at 95° C. for two hours to form the corresponding mono-amide of tetrapropenyl succinic acid. This tetrapropenyl succinic acid mono-amide, diluted with 265.5 gms. of paraffinic oil, was then added at room temperature with stirring to the zinc methylate solution prepared from 23 gms. (1 mole) of metallic sodium in the form of a sodium methylate solution and 88 gms. (0.5 mole+20 gms. excess) of $ZnCl_2$ dissolved in 300 cc. of methanol. The mixture was gradually heated to 165° C. and was held at 165° C. for 1 hour. The reaction product, being viscous at room temperature, was again diluted with 265.5 gms. of paraffinic oil and filtered through "Hyflo" clay. The final product, the methoxy zinc salt of the mono-amide of tetrapropenyl succinic acid, which contained 66⅔ percent paraffinic oil was clear and fluid at room temperature and gave the following analytical results:

Analysis	Estimated	Found
Percent Zn	4.1	3.97
Percent N	0.9	0.88

EXAMPLE 13

A mixture of 133 gms. (0.5 mole) of tetrapropenyl succinic anhydride, 150 gms. (0.5 mole) of "Amine B" and 100 cc. of benzene was heated with stirring at 95° C. for two hours to form the corresponding mono-amide of tetrapropenyl succinic acid. This tetrapropenyl succinic acid mono-amide, diluted with 315.5 gms. of paraffinic oil was then added at room temperature with stirring to the zinc methylate solution prepared from 23 gms. (1 mole) of metallic sodium in the form of a Na methylate solution and 88 gms. (0.5 mole+20 gms. excess) of $ZnCl_2$ dissolved in 300 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 tetrapropenyl succinic acid mono-amide, which contained 50 percent of paraffinic oil, was clear and fluid at room temperature and gave the following results upon analysis:

Analysis	Estimated	Found
Percent Zn	5.05	5.46
Percent N	1.1	0.97

EXAMPLE 14

A mixture of 133 gms. (0.5 mole) of tetrapropenyl succinic anhydride, 100 gms. (0.5 mole) of "Amine A" and 100 cc. of benzene was heated with stirring at 95° C. for two hours to form the corresponding mono-amide of tetrapropenyl succinic acid. This tetrapropenyl succinic mono-amide acid, diluted with 257 gms. of xylene, was then added at room temperature with stirring to 24.32 gms. (1 mole) of Mg in the form of a magnesium methylate solution. The mixture was gradually heated to 120° C. until the methanol and benzene stopped coming over (about one hour). The reaction product, being viscous at room temperature, was again diluted with 257 gms. of xylene and filtered through "Hyflo" clay. The final product, the complex methoxy magnesium salt of the mono-amide of tetrapropenyl succinic acid, which contained 4 Mg equivalents and 66⅔ percent xylene was clear and fluid at room temperature. The product upon analysis gave the following results:

Analysis	Estimated	Found
Percent Mg	3.1	3.08
Percent N	0.9	0.95

EXAMPLE 15

A mixture of 88.7 gms. (⅓ mole) of tetrapropenyl succinic anhydride, 66.7 gms. (⅓ mole) of "Amine A" and 540 gms. of paraffinic oil as diluent was heated at 95–100° C. for three hours with stirring to form the corresponding mono-amide of tetrapropenyl succinic acid. This tetrapropenyl succinic acid mono-amide was then added at room temperature with stirring to 24.32 gms. (1 mole) of Mg in the form of a magnesium methylate solution. The mixture while being heated gradually to distill out the methanol, began to thicken at 80° C. A quantity of 15 cc. of water added dropwise made the reaction mixture fluid again. The reaction mixture was

then gradually heated to 150° C. to complete the reaction and filtered through "Hyflo" clay easily. The final product, the complex methoxy magnesium salt of the mono-amide of tetrapropenyl succinic acid, which contained 6 Mg equivalents and 75 percent paraffinic oil, was clear and fluid at room temperature. Upon analysis this product gave the following results:

Analysis	Estimated	Found
Percent Mg	1.5	1.3
Percent N	0.87	0.8

In order to demonstrate the importance of having the amidic nitrogen atom of the instant metal salts attached to a tertiary carbon atom of a tertiary-alkyl group, tetrapropenyl succinic acid mono-amide metal salts wherein the amidic nitrogen is attached to a non-tertiary carbon atom, were prepared as described in the following Examples 16 and 17.

The normal aliphatic primary amines used in these examples were of commercial quality and are manufactured and sold under the trade names "Armeen C" and "Armeen 18D." "Armeen C" is a mixture of normal aliphatic primary amines containing from 8 to 18 carbon atoms. This mixture contains about 50 percent of dodecyl amine, about 20 percent of tetradecyl, about 10 percent of octyl, decyl and hexadecyl, and less than 10 percent of octadecyl and octadecenyl primary amines. "Armeen 18D" is a mixture of normal primary amines containing about 90 percent of octadecyl with minor amounts of hexadecyl and octadecenyl primary amines.

EXAMPLE 16

A mixture of 133 gms. (0.5 mole) of tetrapropenyl succinic anhydride, 111.5 gms. (0.5 mole) of "Armeen C" and 260 gms. of Process oil (a conventionally refined paraffinic oil having a Saybolt Universal Viscosity of 100 S.U.V. at about 100° F.) as diluent was stirred at 95° C. for two hours to form the "Armeen C" mono-amide of tetrapropenyl succinic acid. To this tetrapropenyl succinic acid mono-amide, 20 gms. (0.5 mole) of NaOH previously dissolved in 300 cc. of methanol was added at room temperature with stirring. The mixture was gradually heated to 175° C. to form the sodium salt. To the sodium salt, 44 gms. (0.25 mole+10 gms. excess) of zinc chloride previously dissolved in 200 cc. of methanol was added at room temperature with stirring. The mixture was gradually heated to 175° C. and was held at 175° C. for one hour. The reaction product was filtered through "Hyflo" clay. The final product, the zinc salt of the "Armeen C" mono-amide of tetrapropenyl succinic acid, which contained 50 percent paraffinic oil was clear and fluid at room temperature and gave the following results upon analysis:

Analysis	Estimated	Found
Percent Zn	3.1	3.75
Percent N	1.35	1.43

EXAMPLE 17

A mixture of 133 gms. (0.5 mole) of tetrapropenyl succinic anhydride, 150 gms. (0.5 mole) of "Armeen 18D," 299 gms. of the paraffinic oil of Example 16 and 100 cc. of benzene was stirred at 95° C. for two hours to form the "Armeen 18D" mono-amide of tetrapropenyl succinic acid. To this tetrapropenyl succinic acid mono-amide, 20 gms. (0.5 mole) of sodium hydroxide previously dissolved in 300 cc. of methanol was added at room temperature with stirring. The mixture was gradually heated to 175° C. to form the sodium salt. To this sodium salt, 44 gms. (0.25 mole+10 gms. excess) of zinc chloride previously dissolved in 200 cc. of methanol was added at room temperature with stirring. The mixture was gradually heated to 175° C. and was held at 175° C. for one hour. The reaction product was filtered through "Hyflo" clay. The final product, the zinc salt of "Armeen 18D" mono-amide tetrapropenyl succinic acid, which contained 50 percent paraffinic oil, was clear and fluid at room temperature and gave the following analytical results:

Analysis	Estimated	Found
Percent Zn	2.7	3.23
Percent N	1.1	1.24

Screen-clogging test.—The anti-screen clogging characteristics of the 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 tarred 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 (milligrams recovered) is converted into percent screen clogging.

Blends of fuel oil (60 percent catalytically cracked component and 40 percent straight run component, approximate boiling range: 320°–640° F.) and the metal salts of the various working examples were prepared and subjected to the aforedescribed test. The results are set forth in Table I.

Table I.—Screen clogging tests

Additive	Conc., lbs. 1,000 bbls.	Screen clogging, percent
Blank (none)	0	100
Example 1	50	11
Example 2	25	12
Example 3	50	77
Example 4	50	25
Example 5	50	34
Example 7	25	20
Example 8	50	23
Example 9	25	75
Example 10	10	13
Example 11	10	6
Example 12	10	30
Example 13	10	20
Example 14	50	5
Example 15	10	4

It will be noted from the data in Table I that the metal salts of tetrapropenyl succinic mono-amide of the present invention are effective anti-screen clogging agents.

Sedimentation test.—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 twelve weeks. Then, the sample is removed from the oven and cooled. The cooled sample is filtered through a tarred 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 said 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.

Additives described in the examples were blended in test fuel oil and the blends were subjected to the 110° F. storage test. The test results comparing the blended fuels and uninhibited fuels are set forth in Table II. The test fuel was a blend of 60 percent catalytically cracked component and 40% straight run component, having a boiling range of approximately 320–640° F.

Table II.—Sedimentation tests

Additive	Conc., lb./1,000 bbls.	Sediment, mg./liter
Blank (fuel oil of boiling range 320°–640° F.)	0	25
Example 1	50	3
Blank	0	25
Example 2	25	3
Blank	0	104
Example 5	50	19
Blank	0	25
Example 6	25	7
Blank	0	25
Example 7	50	4
Blank	0	25
Example 8	25	3
Blank	0	25
Example 9	10	6
Blank	0	89
Example 10	50	24
Blank	0	89
Example 11	50	59
Blank	0	45
Example 14	10	5
Blank	0	77
Example 15	25	19

As will be seen from the data of Table II, the presence of the instant metal salts significantly inhibits the formation of sediment in the fuel oils.

Anti-rust test.—The method used for testing anti-rust properties of both the fuels and turbine oils was the ASTM rust test D–665 operated for 48 hours at 80° F. using distilled water. This is a dynamic test that indicates the ability of fuels to prevent rusting of ferrous metal surfaces in pipelines, tubes, etc., and the ability of turbine oils to aid in preventing the rusting of ferrous parts when water is present with the oil. The test method, in general, involves stirring 300 ml. of the oil under test with 30 ml. of distilled water, while maintaining a cylindrical steel specimen immersed therein. At the end of the test, the specimen is inspected without magnification under normal light (about 60 foot candles) to determine the presence of rust. An oil is reported as passing the test if the steel specimen is rust-free according to this method of observation; while an oil fails the test if the specimen exhibits rust.

The additives described in the examples were added to the test fuels and turbine oils which were then subjected to the Rust Test. The test fuels were a blend of 60 percent catalytically cracked component and 40 percent straight run component having an approximate boiling range of 320–640° F.; while the turbine oils were light turbine oil blends comprising solvent-refined Mid-Continent stock having an S.U.S. at 100° F. of 150 about 0.15 percent dihexyl dithiophosphate, and about 0.25 percent dibutyl para-cresol.

Table III.—ASTM rust test D–665 on fuel oil

Additive	Concn., p.p.m.	Rust test result
Blank (fuel oil of boiling range 320–640° F.)	0	Fail.
Example 3	10	Pass.
Example 4	10	Do.
Example 6	10	Do.
Example 9	10	Do.
Example 11	25	Do.
Example 12	25	Do.
Example 13	25	Do.
Example 15	25	Do.

Table IV.—ASTM rust test D–665 on turbine oil

Additive	Concn., wt. percent	Rust test result
Blank (light turbine oil)	0	Fail.
Example 1	0.1	Pass.
Example 2	0.1	Do.
Example 3	0.1	Do.
Example 4	0.1	Do.
Example 5	0.1	Do.
Example 6	0.1	Do.
Example 7	0.1	Do.
Example 8	0.1	Do.
Example 9	0.1	Do.
Example 10	0.1	Do.
Example 11	0.1	Do.
Example 12	0.15	Do.
Example 13	0.1	Do.
Example 15	0.1	Do.

Tin-babbitt corrosion tests.—The ability of the additives of the present invention to inhibit tin-babbitt corrosion in lubricating oil compositions such as turbine oils is shown in the following tests.

The various metal salts of the working examples were added to a heavy turbine oil blend comprising a solvent-refined Kuwait stock (about 420 S.U.S. at 100° F.), 0.15 percent zinc dihexyl dithiophosphate, 0.19 percent complex carbonated barium nonylphenate sulfide containing 10 percent by weight barium, and 0.25 percent dibutyl para cresol.

A tin-babbitt (approximately 83 percent tin, 8 percent copper, 8 percent antimony, and 1 percent miscellaneous metals) coupon (1" x 11/16" x 1/8") was wedged in a suitable "Teflon" holder and placed in a 200 ml. beaker. A small volume (up to 1.0 ml.) of electrolyte (e.g., synthetic sea water) was placed on the babbitt coupon. 100 ml. of the turbine oil was added while carefully maintaining the electrolyte on the coupon. The beaker was then placed in a forced draft over and heated to a temperature of 240° F. for 100 hours. Make-up synthetic sea water was added every twenty-four hours.

The babbitt was then removed and the surface thereof subjected to X-ray diffraction analysis to determine the presence of stannous oxide and stannic oxide. Essentially, this analysis procedure relies on the intensities of the reflected X-rays increasing suddenly at angles characteristic of the particular oxides present. These abrupt changes on intensities are traced as peaks. The heights of these peaks, measured as the number of horizontal grid lines forming the peak, are taken to be proportional to the amount of oxide under the beam.

The test results are reported in the following Table V.

Table V.—Tin babbitt corrosion tests

Additive	Conc., wt. percent	Oxide Formation	
		Stannic oxide	Stannous oxide
Blank (heavy turbine oil blend)	0	7	15
Example 2	0.1	0	8
Example 3	0.1	0	8
Example 4	0.1	0	0
Example 5	0.1	0	0
Example 7	0.1	0	8
Example 10	0.1	0	0
Example 11	0.1	0	6
Example 12	0.1	0	0
Example 13	0.1	0	0

It will be noted from the data of Table V that the metal salts of the present invention effectively inhibit tin-babbitt corrosion as indicated by their ability to cut down or completely reduced the amounts of stannous and stannic oxides formed on the babbitt surfaces.

Emulsion tests.—Turbine oils containing the metal salts of Example 3, 4, 16, and 17 were evaluated in the ASTM D1401–56T emulsion test for steam turbine oils.

This test, which measures the ability of the oil and water to separate from each other, is carried out by stir-

ring a mixture containing 40 ml. of the oil sample and 40 ml. of distilled water for five minutes at 130° F. in a graduated cylinder. The amounts of emulsion (ml.) remaining after thirty minutes is then recorded.

The metal salts of the working examples were added to a heavy turbine oil blend comprising a solvent-refined Kuwait stock having an S.U.S. at 100° F. of about 420, about 0.15 percent zinc dihexyl dithiophosphate, about 0.19 percent complex carbonated barium nonylphenate sulfide containing 10 percent by weight barium and about 0.25 percent dibutyl para-cresol.

For the purposes of the test an oil is considered to possess suitable demulsibility characteristics if no more than 15–20 ml. of emulsion remain.

The results are reported in Table VI.

Table VI.—Oil emulsion tests ASTM D1401–56T

Additive	Conc. Wt., percent	Ml. Emulsion at 30 min.
Blank (heavy turbine oil)	0	3
Example 3	0.2	5
Example 4	0.2	7
Example 16	0.2	56
Example 17	0.2	28

It will be noted from Table VI that the turbine oils containing as an additive, the metal salts of tetrapropenyl succinic acid mono-amide, wherein the amidic nitrogen is derived from a straight chain amine (Examples 16 and 17), exhibited such poor demulsibility characteristics that they failed the test. By contrast, the turbine oils containing the metal salts of the instant invention, wherein the amidic nitrogen is attached to a tertiary carbon atom of a tertiary-alkyl group (Examples 3 and 4), exhibited good demulsibility characteristics and passed the test.

Although the present invention has been described with certain preferred embodiments, it is to be understood that modifications and variations may, of course, be resorted to without departing from the spirit and scope of the invention.

Having thus described the invention, what we desire to secure and claim by Letters Patent is:

1. A composition comprising a major proportion of a base fluid selected from the group consisting of hydrocarbon lubricating oils and hydrocarbon fuel oils and a minor proportion sufficient to improve the anti-screen clogging, sediment-stabilization and anti-rust characteristics of the composition of a metal salt of a mono-amide of tetrapropenyl succinic acid with at least one of a tertiary-alkyl primary amine having a tertiary carbon attached to the nitrogen atom, the metal component of said metal salt being selected from the class consisting of Groups II and III of the Mendeleeff Periodic Table.

2. The composition of claim **1**, wherein the tertiary-alkyl primary amine contains about 4 to about 30 carbon atoms per tertiary-alkyl radical.

3. The composition of claim **1**, wherein the tertiary-alkyl primary amine contains from about 12 to about 15 carbon atoms per tertiary-alkyl radical.

4. The composition of claim **1**, wherein the tertiary-alkyl primary amine contains from about 18 to about 24 carbon atoms per tertiary-alkyl radical.

5. The composition of claim **1**, wherein the tertiary-alkyl primary amine contains 12 carbon atoms.

6. The composition of claim **1**, wherein the tertiary-alkyl primary amine contains 18 carbon atoms.

7. The composition of claim **1**, wherein the metal component of said metal salt is calcium.

8. The composition of claim **1**, wherein the metal component of said metal salt is magnesium.

9. The composition of claim **1**, wherein the metal component of said metal salt is zinc.

10. The composition of claim **1**, wherein the metal component of said metal salt is barium.

11. The composition of claim **1**, wherein the metal component of said metal salt is aluminum.

12. A fuel composition comprising a major proportion of a hydrocarbon fuel oil and a minor proportion, sufficient to improve the anti-screen clogging, sediment-stabilization and anti-rust characteristics of the composition of a metal salt of a mono-amide of tetrapropenyl succinic acid with at least one of a tertiary-alkyl primary amine having a tertiary carbon attached to the nitrogen atom, the metal component of said metal salt being selected from the class consisting of Groups II and III of the Mendeleeff Periodic Table.

13. The fuel composition of claim **12**, wherein said metal salt is present in a proportion from about 1 to about 200 pounds per thousand barrels of hydrocarbon fuel.

14. A lubricating composition comprising a major proportion of a hydrocarbon lubricating oil and a minor proportion, sufficient to improve the anti-rust, anti-tin-babbitt corrosion and demulsibility characteristics of the composition, a metal salt of a mono-amide of tetrapropenyl succinic acid with at least one of a tertiary-alkyl primary amine having a tertiary carbon attached to the nitrogen atom, the metal component of said metal salt being selected from the class consisting of Groups II and III of the Mendeleeff Periodic Table.

15. The lubricating composition of claim **14**, wherein said metal salt is present in a proportion from about 0.001 percent to about 1.0 percent by weight.

16. The lubricating composition of claim **14**, wherein said metal salt is present in a proportion from about 0.01 percent to about 0.05 percent by weight.

17. A turbine lubricating oil composition comprising a major proportion of a hydrocarbon lubricating oil and a minor proportion, sufficient to improve the anti-rust, anti-tin-babbitt corrosion and demulsibility characteristics of the composition of a metal salt of a mono-amide of tetrapropenyl succinic acid with at least one of a tertiary-alkyl primary amine containing from about 4 to about 30 carbon atoms per tertiary-alkyl radical and having a tertiary carbon attached to the nitrogen atom, the metal component of said metal salt being selected from the class consisting of Groups II and III of the Mendeleeff Periodic Table.

18. The turbine oil lubricating composition of claim **17**, wherein the tertiary-alkyl primary amine contains from about **12** to about **15** carbon atoms per tertiary-alkyl radical.

19. The turbine oil lubricating composition of claim **17**, wherein the tertiary-alkyl primary amine contains from about 18 to about 24 carbon atoms per tertiary-alkyl radical.

20. The turbine oil lubricating composition of claim **17**, wherein the metal component of said metal salt is zinc.

References Cited by the Examiner

UNITED STATES PATENTS

2,458,425	1/1949	Rocchini	252—33.6
2,699,427	1/1955	Smith et al.	44—71
3,039,861	6/1962	Andress et al.	44—71
3,046,102	7/1962	Andress et al.	44—71
3,121,057	2/1964	Gee et al.	252—33.6

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