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ALKOXY METAL SALTS OF SUCCINAMIC ACIDS

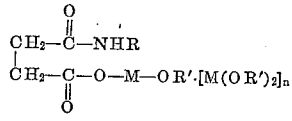
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3 Claims. (Cl. 260—429)

ABSTRACT OF THE DISCLOSURE

Metal salts of succinamic acids are provided which are effective for inhibiting petroleum distillate fuel oils against sedimentation, screen clogging, emulsification and rusting of ferrous metal surfaces in contact therewith. These metal salts have the following formula:



wherein R is a monovalent aliphatic hydrocarbon group having between 4 and 30 carbon atoms and a tertiary carbon atom linked to the nitrogen atom; R′ is a saturated aliphatic hydrocarbon group; M is a divalent metal; and *n* is an integer of 0 to 10.

This invention is a division of our copending application Ser. No. 208,127, filed July 6, 1962, now Patent No. 3,264,075, issued Aug. 2, 1966, and relates to the improvement of non-lubricating petroleum fractions. It is more particularly concerned with distillate fuel oils containing additives adapted to inhibit the appearance of sediment during prolonged storage periods, to prevent screen-clogging, prevent rusting of ferrous metal surfaces, and to inhibit the fuel oils against 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.

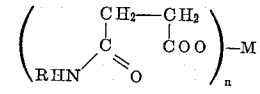
Generally, it has been the practice to overcome the aforedescribed difficulties with a separate additive for each purpose, i.e., with a sediment inhibitor, an anti-screen clogging agent, and an antirust agent. The use of several additives, however, gives rise to problems of additive compatability, thus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

It has now been found that all three problems, i.e., sedimentation, screen clogging, and rusting, can be solved by the use of a single fuel oil addition agent. It has been discovered that a distillate fuel oil containing minor amounts of certain metal salts of certain amic acids are

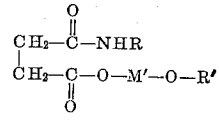
effectively inhibited, simultaneously, against all three aforementioned difficulties and of considerable importance, without inducing objectionable emulsification characteristics to the distillate fuel oils.

Accordingly, it is a broad object of this invention to provide a fuel oil having properties improved with a minimum number of addition agents. Another object is to provide a fuel oil having a single additive adapted to inhibit sedimentation, to prevent screen clogging, and to prevent rusting of ferrous metal surfaces with which it comes in contact. A specific object is to provide a fuel oil containing certain metal salts of amic acids that achieves these results. Other objects and advantages of this invention will become apparent to those skilled in the art from the following detailed description.

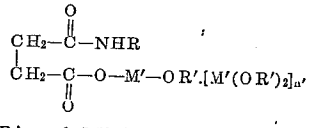
The present invention provides a distillate fuel oil containing a minor amount, sufficient to inhibit sedimentation and screen clogging, and to prevent rusting of ferrous metal surfaces in contact therewith without inducing objectionable emulsification characteristics to said fuel oil, of a compound selected from the group consisting of (1) a metal salt of a succinamic acid having the formula:

I 

wherein R is a monovalent aliphatic hydrocarbon radical having between about 4 and about 30 carbon atoms and a tertiary carbon atom linked to the nitrogen atom; M is a metal selected from the group consisting of divalent copper, and metals from Groups II–A, II–B, III–A, IV–A, and VIII of the Periodic Chart of the Elements and *n* is a small whole number equal to the valence of M; (2) an alkoxy metal salt of succinamic acid having the formula:

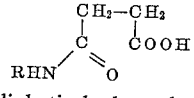
II 

wherein R′ is a saturated aliphatic hydrocarbon group preferably from 1 to 18 carbon atoms, M′ is a divalent metal, R has the aforesaid significance; and (3) complex alkoxy metal salts of succinamic acid having the formula:

III 

wherein R, R′ and M′ have the aforesaid significance, and *n′* is an integer of 1 to 5, or more, such as 1 to 10, and preferably 1 to 6.

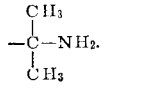
The addition agents utilizable in the fuel oil compositions of this invention are metal salts of amic acids that have the formula:



wherein R is an aliphatic hydrocarbon radical of an aliphatic, primary tertiary alkyl amine containing between about 4 and about 30 carbon atoms and a tertiary carbon atom attached to the nitrogen atom. The amic acids contemplated herein can be made by any method for preparing such compounds that is known to the art. They are produced, preferably, by warming succinic acid anhydride with a primary tertiary-alkyl amine having between about 4 and about 30 carbon atoms per molecule to form the monoamide of the acid. This can be done readily by heating the mixture of anhydride and amine at a temperature of 65–150° C. for a period of time varying between one

and 3 hours. The addition occurs readily without the formation of water. Less desirably, the amic acids can be prepared by the controlled reaction between succinic acid and the amine, with the elimination of one mole of water per mole of amic acid produced. Care must be exercised to avoid the elimination of two moles of water to form the cyclic imide.

The amines that can be utilized to form the amic acids are the tertiary alkyl, primary, monoamines in which a primary amino (—NH_2) group is attached to a tertiary carbon atom; and mixtures thereof. These amines all contain the terminal group,



Non-limiting examples of the amine reactants are t-butyl primary amine, t-hexyl primary amine, t-octyl primary amine, t-decyl primary amine, t-dodecyl primary, amine, t-tetradecyl primary amine, t-octadecyl primary amine, t-eicosyl primary amine, t-tetracosyl primary amine, and t-triacontyl primary amine. The amine reactants can be prepared in several ways well known to those skilled in the art. Specific methods of preparing the t-alkyl primary amines are disclosed in the Journal of Organic Chemistry, vol. 20, p. 295 at seq. (1955). Mixtures of such amines can be made from a polyolefin fraction (e.g., polypropylene and polybutylene cuts) by first hydrating with sulfuric acid and water to the corresponding alcohol, converting the alcohol to alkyl chloride with ammonia, under pressure, to produce the t-alkyl primary amine mixture.

The salts of the succinamic acids contemplated herein are metal salts wherein the salt-forming metal is an appropriate metal from Groups I–B, II–A, II–B, III–A, IV–A and VIII of the Periodic Chart of the Elements, as set forth in "Introductory College Chemistry" by H. G. Deming (John Wiley and Sons). Preferred salt-forming metals are cupric Cu, Ba, Ca, Sr, Mg, Zn, Cd, Al, Pb and Fe. The method of forming the metal salts of this invention is not a critical factor herein. Thus, any of the usual methods known to those skilled in the art can be utilized. Typical methods for forming the normal salt (Formula I) include forming an alkali-metal salt (e.g., by neutralizing with caustic), and then using a double decomposition reaction with a salt of the desired metal (e.g., $CuSo_4$); neutralizing the acid with a metal alcoholate (e.g., barium methylate); and heating with an oxide of the metal (e.g., magnesium oxide). Suitably, the non-polar solvents can be used in the salt-forming operation. In many cases, the metal salts of this invention can be used in solution in the solvent, for greater ease of handling. Thus, concentrates of the salts of this invention in amounts varying between 10% and about 90%, by weight, in a solvent are contemplated. Such concentrates are then added to the fuel oil to give the desired final concentration in the fuel. Suitable solvents are benzene, toluene, xylene, light lubricating oil, Sovasol #5 and kerosene. The alkoxy metal salts (Formula II) can be prepared by heating one mole of the succinamic acid with one mole of an appropriate $M(O\text{-alkyl})_2$ compound (e.g., magnesium methylate); and the complex alkoxy metal salts (Formula III) can be prepared by heating the succinamic acid with two or more moles of the stated $M(O\text{-alkyl})_2$ compound.

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 narower 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 as heating and diesel fuel oils, and 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 metal salt of succinamic acid that is added to the distillate fuel oil in accordance with this invention will depend upon the intended purpose and the particular amic acid salt selected, as they are not all equivalent in their activities. Some may have to be used to be used in greater concentrations than others to be effective. In most cases, in which it is desired to obtain all three beneficial results, namely, to inhibit sedimentation, to reduce screen clogging, and to prevent rusting of ferrous metal surfaces, 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 three 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 amic 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.

The following specific examples are for the purpose of illustrating the fuel 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 fuel oils, or to the operations and manipulations described therein. Other amic acid salts and fuel oils, as discussed hereinbefore, can be used, as those skilled in the art will readily appreciate.

The amine reactants used in the specific 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 12 carbon atoms per molecule. This mixture contains, by weight, about 85 percent tertiarydodecyl primary amine, about 10 percent tertiary-pentadecyl primary 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 mixture of tertiary-alkyl primary amines containing 18 to 24 carbon atoms per molecule and averaging about 20 carbon atoms per molecule. It has a tertiary carbon atom attached to the $—NH_2$ group and contains, 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.

In the following examples, solvents were used to facilitate handling the products. Among the solvents used herein are "Sovasol #5" and a "light lubricating oil." Sovasol #5 is an aliphatic petroleum solvent having a boiling range of 320–381° F., an API Gravity of 45.5°, and an Aniline Point of 112° F. The "light lubricating oil" is a solvent-refined paraffinic oil having an API Gravity of 33°, a pour point of 20° F., a viscosity of 128 seconds Saybolt at 100° F., and a Viscosity Index of 105.

Example 1

A mixture of 50 gms. (0.5 mole) of succinic anhydride, 100 gms. (0.5 mole) of Amine A and 300 gms. of Sovasol #5 as a diluent was stirred at 85–100° C. for approximately 2 hours to form the Amine A succinamic acid. To the above Amine A succinamic acid was added at room temperature with stirring 69 gms. (0.25 mole+6 gms. excess) of $CuSO_4.5H_2O$ previously dissolved in 100 cc. of water and then 21 gms. (0.5 mole+1 gm. excess) of NaOH previously dissolved in 100 cc. of water. The mixture was stirred at 100° C. for 6 hours. The reaction product was separated from the water layer and filtered by gravity. The final product, the copper salt of the Amine A succinamic acid, which contained 66⅔% Sovasol #5 was fluid at room temperature.

Analysis.—Cu, 1.72%; N, 1.32%.

Example 2

A mixture of 50 gms. (0.5 mole) of succinic anhydride, 100 gms. (0.5 mole) of Amine A and 100 cc. of benzene as a diluent was stirred at 85° C. for 2 hours to form the Amine A succinamic acid. The Amine A succinamic acid was then added at room temperature with stirring to 6 gms. (0.25 mole) of Mg in the form of a Mg methylate solution. The mixture was gradually heated to 150° C. to distill out the methanol. The reaction product, the Mg salt of Amine A succinamic acid, being viscous, was diluted with 312 gms. of xylene and filtered through filtering clays. The final product which contained 66⅔% xylene was clear and fluid at room temperature.

Analysis.—Estimated: Mg, 1.28%; N, 1.50%. Found: Mg, 1.28; N, 1.59.

Example 3

A mixture of 50 gms. (0.5 mole) of succinic anhydride, 100 gms. (0.5 mole) of Amine A and 150 cc. of xylene as a diluent was stirred at 95° C. for 2 hours to form the Amine A succinamic acid. To the above Amine A succinamic acid was added at room temperature with stirring 286 gms. of 12% Ba methylate solution (equivalent to 0.25 mole of Ba). The mixture was gradually heated to 175° C. to distill out the solvent. The reaction product, the Ba salt of Amine A succinamic acid, being viscous, was diluted with 736 gms. of xylene and filtered through filtering clay. The final product which contained approximately 80% xylene was clear and fluid at room temperature.

Analysis.—Estimated: Ba, 3.2%; N, 0.7%. Found: Ba, 2.98%; N, 0.72%.

Example 4

A mixture of 50 gms. (0.5 mole) of succinic anhydride, 100 gms. (0.5 mole) of Amine A and 200 cc. of toluene was stirred at 85° C. for 2 hours to form the Amine A succinamic acid. To the above Amine A succinamic acid was added at room temperature with stirring 20 gms. (0.5 mole) of NaOH dissolved in 200 cc. of methanol. The mixture was gradually heated to 175° C. to form the sodium salt of Amine A succinamic acid. To the sodium salt of Amine A succinamic acid was then added at room temperature 33 gms. (0.25 mole+5 gms. excess) of $CaCl_2$ previously dissolved in 200 cc. of methanol. The mixture was gradually heated to 175° C. to form the Ca salt. The reaction product being viscous, was diluted with 200 cc. of benzene, filtered through filtering clay and topped to 175° C. under house vacuum. The final product, the Ca salt of Amine A succinamic acid, weighed 150 gms. and was diluted with 150 gms. of xylene.

Analysis.—Estimated: Ca, 3.15%; N, 2.2%. Found: Ca, 3.23%; N, 2.28%.

Example 5

A mixture of 50 gms. (0.5 mole) of succinic anhydride, 100 gms. (0.5 mole) of Amine A and 150 cc. of xylene was stirred at 95° C. for 2 hours to form the Amine A succinamic acid. To the above Amine A succinamic acid was added at room temperature with stirring 20 gms. (0.5 mole) of NaOH dissolved in 200 cc. of methanol. The mixture was gradually heated to 175° C. to form a sodium salt of the Amine A succinamic acid. To the sodium salt of Amine A succinamic acid was then 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. to form a Zn salt of the Amine A succinamic acid. The reaction product was diluted with 500 cc. of benzene, filtered through filtering clay and topped to 100° C. under house vacuum to remove the benzene. The final product, the Zn salt of the Amine A succinamic acid, which weighed 156 gms. was viscous and diluted with 156 gms. of xylene.

Analysis.—Estimated: Zn, 5.02%; N, 2.10%. Found: Zn, 5.05%; N, 1.90%.

Example 6

A mixture of 50 gms. (0.5 mole) of succinic anhydride, 100 gms. (0.5 mole) of Amine A and 100 cc. of toluene was stirred at 95° C. for 2 hours to form the Amine A succinamic acid. To the above Amine A succinamic 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 150° C. and was held at 150° C. for 2 hours to insure the complete formation of the sodium salt of the Amine A succinamic acid. To the sodium salt of the Amine A succinamic acid was then added at room temperature with stirring 30 gms. (⅙ mole+3 gms. excess) of ferric chloride dissolved in 200 cc. of methanol. The mixture was gradually heated to 150° C. and was held at 150° C. for 3 hours. The reaction product was diluted with 200 cc. of benzene, filtered through filtering clay and topped to 60° C. under a pressure of 3 mm. of mercury. The final product, the iron salt of Amine A succinamic acid, which weighed 147 gms. was viscous at room temperature and diluted with 147 gms. of xylene.

Analysis.—Estimated: Fe, 2.9%; 2.2%. Found: Fe, 3.42%; 2.25%.

Example 7

A mixture of 50 gms. (0.5 mole) of succinic anhydride, 100 gms. (0.5 mole) of Amine A and 150 cc. of xylene was stirred at 95° C. for 2 hours to form the Amine A succinamic acid. To the above Amine A succinamic acid was added at room temperature with stirring 4.5 gms. (⅛ mole) of aluminum in the form of an aluminum butylate solution. The mixture was gradually heated to 175° C. to form the aluminum salt of the Amine A succinamic acid. The reaction product was diluted with 500 cc. of benzene, filtered through filtering clay and topped to 150° C. under the house vacuum. The

final product which weighed 130 gms. was viscous and diluted with 130 gms. of xylene.

Analysis.—Estimated: Al, 1.4%; N, 2.3%. Found: Al, 1.25%; N, 2.37%.

Example 8

A mixture of 50 gms. (0.5 mole) of succinic anhydride, 150 gms. (0.5 mole) of Amine B and 150 cc. of xylene was stirred at 95° C. for 4 hours to form the Amine B succinamic acid. To the above Amine B succinamic acid was added at room temperature with stirring 6 gms. (0.25 mole) of Mg in the form of a Mg methylate solution. The mixture was gradually heated to 175° C. to form the Mg salt of Amine B succinamic acid. The reaction product being viscous, was diluted with 206 gms. of light lubricating oil and filtered through filtering clay.

Analysis.—Estimated: Mg, 1.34%; N, 1.7%. Found: Mg, 1.49%; N, 1.87%.

Example 9

A mixture of 50 gms. (0.5 mole) of succinic anhydride, 150 gms. (0.5 mole) of Amine B and 150 cc. of xylene was stirred at 95° C. for 2 hours to form the Amine B succinamic acid. To the above Amine B succinamic acid was added at room temperature with stirring 20 gms. (0.5 mole) NaOH previously dissolved in 200 cc. of methanol. The mixture was gradually heated to 175° C. to form the sodium salt of the Amine B succinamic acid. To the Na salt of the Amine B succinamic acid was then added 420 gms. of light lubricating oil and 33 gms. (0.25 mole+5 gms. excess) of $CaCl_2$ previously dissolved in 200 cc. of methanol. The mixture was gradually heated to 175° C. and was held there for 3 hours to insure the complete formation of the Ca salt. The reaction product was filtered through filtering clay. The final product, the calcium salt of the Amine B succinamic acid, which contains 66⅔% light lubricating oil was fluid at room temperature.

Analysis.—Estimated: Ca, 1.85%; N, 1.32%. Found: Ca, 1.57%; N, 1.12%.

Example 10

A mixture of 50 gms. (0.5 mole) of succinic anhydride. 150 gms. (0.5 mole) of Amine B and 150 cc. of toluene was stirred at 95° C. for 2 hours to form the Amine B succinamic acid. To the above Amine B succinamic acid was added at 50° C. with stirring 286 gms. of 12% Ba methylate solution (0.25 mole of Ba). The mixture was gradually heated to 175° C. The reaction product being viscous, was diluted with 468 gms. of light lubricating oil and filtered through filtering clay. The final product, the Ba salt of the Amine B succinamic acid, which contained 66⅔% light lubricating oil, was fluid at room temperature.

Analysis.—Estimated: Ba, 4.8%; N, 0.9%. Found: Ba, 2.33%; N, 0.86%.

Example 11

A mixture of 50 gms. (0.5 mole) of succinic anhydride, 150 gms. (0.5 mole) of Amine B and 150 cc. of xylene was stirred at 95° C. for 2 hours to form the Amine B succinamic acid. To the above Amine B succinamic acid was added at room temperature with stirring 20 gms. (0.5 mole) of NaOH previously dissolved in 250 cc. of methanol. The mixture was gradually heated to 175° C. to form the Na salt of the Amine B succinamic acid. To the Na salt of the Amine B succinamic acid was then added at room temperature with stirring 432 gms. of light lubricating oil and 44 gms. (0.25 mole+10 gms. excess) of $ZnCl_2$ previously dissolved in 250 cc. of methanol. The mixture was gradually heated to 175° C. and was held at 175° C. for 3 hours to insure the complete formation of the Zn salt of the Amine B succinamic acid. The product was filtered through filtering clay. The final product which contained 66⅔% light lubricating oil was fluid at room temperature.

Analysis.—Estimated: Zn, 2.5%; N, 1.08%. Found: Zn, 2.91%; N, 1.08%.

Example 12

A mixture of 50 gms. (0.5 mole) of succinic anhydride, 150 gms. (0.5 mole) of Amine B, 206 gms. of light lubricating oil and 100 cc. of benzene was stirred at 95–100° C. for 2 hours to form the Amine B succinamic acid. To the above Amine B succinamic acid was added at room temperature with stirring 10.08 gms. (0.25 mole) of MgO previously mixed with 20 cc. of water to form a paste. The mixture was gradually heated to 175° C. and was held at 175° C. for 2 hours. The reaction product was then filtered through filtering clay. The final product, the Mg salt of the Amine B succinamic acid, which contained 50% light lubricating oil was fluid at room temperature.

Analysis.—Estimated: Mg, 1.4%; N, 1.7%. Found: Mg, 1.24%; N, 1.58%.

Example 13

A mixture of 50 gms. (0.5 mole) of succinic anhydride, 150 gms. (0.5 mole) of Amine B, 206 gms. of light lubricating oil and 100 cc. of benzene was stirred at 100° C. for 2 hours to form the Amine B succinamic acid. To the above Amine B succinamic acid was added at room temperature with stirring 14.6 gms. (0.25 mole) of $Mg(OH)_2$. The mixture was gradually heated to 175° C. and was held at 175° C. for 30 minutes. The product was then filtered through filtering clay. The final product, the Mg salt of Amine B succinamic acid, which contained 50% light luibricating oil was fluid at room temperature.

Analysis.—Estimated: Mg, 1.4%; N, 1.7%. Found: Mg, 1.28%; N, 1.52%.

Example 14

A mixture of 50 gms. (0.5 mole) of succinic anhydride, 150 gms. (0.5 mole) of Amine B and 250 cc. of xylene was stirred at 95° C. for 2 hours to form the Amine B succinamic acid. The Amine B succinamic acid was then added at room temperature with stirring to 11.5 gms. (0.5 mole) of Na in the form of a Na methylate solution. The mixture was gradually heated to 150° C. and was held at 150° C. for 2 hours to insure the complete formation of the Na salt of Amine B succinamic acid. The Na salt, diluted with 750 cc. of benzene, was then added at room temperature with stirring to 76.5 gms. (0.25 mole+7 gms. excess) of $PbCl_2$ dissolved in 2500 cc. of distilled water. The mixture was stirred at 100° C. for 8 hours to insure the complete formation of the lead salt. The lead salt was separated from the water layer, filtered through Hyflo clay and topped to 150° C. under house vacuum. The final product, the lead salt of Amine B succinamic acid, which weighed 228 gms., theory 252 gms. was viscous at room temperature and diluted with 228 gms. of xylene.

Analysis.—Estimated: Pb, 10.0%; N, 1.3%. Found: Pb, 9.7%; N, 1.53%.

Example 15

A mixture of 150 gms. (0.5 mole) of Amine A succinamic acid, diluted with 150 gms. of Solvesso #150, and 12 gms. (0.5 mole) of Mg in the form of a Mg methylate solution was gradually heated to 150° C. to remove the methanol. The reaction product, being viscous, was diluted with 150 gms. of toluene and filtered through Hyflo clay. The final product, the methoxy Mg salt of Amine A succinamic acid, which contained 66⅔% solvent was clear and fluid at room temperature.

Analysis.—Estimated: Mg, 2.6%. Found: Mg, 2.8%.

Example 16

A mixture of 50 gms. (0.5 mole) of succinic anhydride and 150 gms. (0.5 mole) of Amine B was heated with stirring at 100–105° C. for 1½ hours to form the Amine B succinamic acid. The Amine B succinamic acid, diluted

with 600 gms. of Solvesso #150, was added at room temperature with stirring to 24.32 gms. (1 mole) of Mg in the form of a Mg methylate solution. The mixture was gradually heated with stirring. At 82° C. the reaction mixture started to thicken but became fluid after a quantity of 15 cc. of water was added. The reaction mixture was then heated to 130° C. to remove the methanol. The final product, the complex methoxy Mg salt of Amine B succinamic acid, which contained 4 equivalents of Mg and 73% Solvesso #150 was clear and fluid at room temperature.

Analysis.—Estimated: Mg, 2.9%. Found: Mg, 2.81%.

Example 17

A mixture of 150 gms. (0.5 mole) of Amine A succinamic acid, diluted with 450 gms. of Solvesso #150, and 24.32 gms. (1 mole) of Mg in the form of a Mg methylate solution was gradually heated to 120° C. to remove the methanol. The final product, the complex methoxy Mg salt of Amine A succinamic acid, which contained 4 Mg equivalents and 72% Solvesso #150 was clear and fluid at room temperature.

Analysis.—Estimated: Mg, 3.8%. Found: Mg, 3.38%.

Example 18

A mixture of 50 gms. (0.5 mole) of succinic anhydride, 150 gms. (0.5 mole) of Amine B and 600 gms. of Solvesso #150 as a diluent was heated with stirring at 95–105° C. for 2 hours to form the Amine B succinamic acid. The Amine B succinamic acid was then added at room temperature with stirring to 36.5 gms. (1.5 mole) of Mg in the form of a Mg methylate solution. The mixture was gradually heated with stirring. At 80° C. the the mixture started to thicken but became fluid after a quantity of 15 cc. of water had been added. The reaction mixture was then gradually heated to 130° C. to remove the methanol. The final product, the complex methoxy Mg salt of Amine B succinamic acid which contained 6 Mg equivalents and 72% Solvesso #150 was clear and fluid at room temperature.

Analysis.—Estimated: Mg, 4.3%. Found: Mg, 4.02%.

Example 19

A mixture of 150 gms. (0.5 mole) of Amine A succinamic acid, diluted with 450 gms. of Solvesso #150, and 36.48 gms. (1.5 moles) of magnesium in the form of a Mg methylate solution was gradually heated with stirring. At 82° C. before thickening occurred, a quantity of 20 cc. of water was added dropwise to the mixture. The mixture was then gradually heated to 125° C. to remove the methanol. The final product, the complex methoxy Mg salt of Amine A succinamic acid, which contained six Mg equivalents and 72% Solvesso #150 was clear and fluid at room temperature.

Analysis.—Estimated: Mg, 5.7%. Found: Mg, 5.42%.

SEDIMENTATION

The test used to determine the sedimentation characteristics of the fuel oils is the 100° 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.

Example 20

Additives described in the foregoing examples were blended in test fuel oils 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 I. The test fuel oil is a blend of 60 percent distillate stock obtained from continuous catalytic cracking and 40 percent straight-run distillate stock. It has a boiling range of between about 320° F. and about 640° F. and is a typical No. 2 fuel oil.

TABLE I.—FUEL OIL STORAGE TEST, TWELVE WEEKS' STORAGE AT 100° F.

Inhibitor	Concn., lb./1,000 bbls.	Sediment, mg./liter
Uninhibited fuel blend	0	104
Uninhibited fuel blend+Ex. 2	50	26
Uninhibited fuel blend	0	100
Uninhibited fuel blend+Ex. 3	50	18
Uninhibited fuel blend	0	104
Uninhibited fuel blend+Ex. 8	50	24
Uninhibited fuel blend	0	100
Uninhibited fuel blend+Ex. 9	50	94
Uninhibited fuel blend	0	100
Uninhibited fuel blend+Ex. 10	50	41
Uninhibited fuel blend	0	25
Uninhibited fuel blend+Ex. 11	10	18
Uninhibited fuel blend	0	79
Uninhibited fuel blend+Ex. 12	50	24
Uninhibited fuel blend	0	79
Uninhibited fuel blend+Ex. 13	50	35
Uninhibited fuel blend	0	10
Uninhibited fuel blend+Ex. 14	25	5
Uninhibited fuel blend	0	79
Uninhibited fuel blend+Ex. 15	50	2
Uninhibited fuel blend	0	46
Uninhibited fuel blend+Ex. 18	10	9
Uninhibited fuel blend	0	46
Uninhibited fuel blend+Ex. 19	25	6

SCREEN CLOGGING

The anti-screen clogging characteristics of a fuel oil were determined as follows: The test is conducted using a Sunstrand 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 crucile 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.

Example 21

Using the test fuel oil described in Example 20, blends of additives from the foregoing examples in this fuel were prepared. Each blend was subjected to the Screen Clogging Test, as aforedescribed. Test results are set forth in Table II.

TABLE II.—SCREEN CLOGGING TESTS

Inhibitor	Concn., lb/1,000 bbls.	Screen Clogging, Percent
Uninhibited fuel blend	0	100
Uninhibited fuel blend+Ex. 1	25	9
Uninhibited fuel blend+Ex. 2	25	27
Uninhibited fuel blend+Ex. 3	50	7
Uninhibited fuel blend+Ex. 4	10	10
Uninhibited fuel blend+Ex. 5	50	21
Uninhibited fuel blend+Ex. 6	50	47
Uninhibited fuel blend+Ex. 7	25	30
Uninhibited fuel blend+Ex. 8	25	27
Uninhibited fuel blend+Ex. 9	50	23
Uninhibited fuel blend+Ex. 10	10	9
Uninhibited fuel blend+Ex. 11	25	24
Uninhibited fuel blend+Ex. 12	25	2
Uninhibited fuel blend+Ex. 13	25	3
Uninhibited fuel blend+Ex. 14	50	9
Uninhibited fuel blend+Ex. 15	50	2
Uninhibited fuel blend+Ex. 18	10	2
Uninhibited fuel blend+Ex. 19	10	5

RUSTING

The method used for testing anti-rust properties of the fuel oils was ASTM Rust Test D-665 operated for 48 hours at 80° F. using distilled water. This is a dynamic test that indicates the ability to prevent rusting of ferrous metal surfaces in pipelines, tubes, etc.

Example 22

Blends of additives described in Examples 1 through 15 in the fuel oil of Example 20 were subjected to the ASTM Rust Test D-665. Pertinent data are set forth in Table III.

TABLE III.—ASTM RUST TEST D-665

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	5	Do.
Blank fuel blend+Ex. 5	10	Do.
Blank fuel blend+Ex. 6	10	Do.
Blank fuel blend+Ex. 7	10	Do.
Blank fuel blend+Ex. 8	10	Do.
Blank fuel blend+Ex. 9	25	Do.
Blank fuel blend+Ex. 10	25	Do.
Blank fuel blend+Ex. 11	25	Do.
Blank fuel blend+Ex. 12	10	Do.
Blank fuel blend+Ex. 13	10	Do.
Blank fuel blend+Ex. 14	25	Do.
Blank fuel blend+Ex. 15	5	Do.

It will be apparent, from the data set forth in Tables I through III, that the metal salts of the succinamic acids of this invention are highly effective to reduce sedimentation and screen clogging and to inhibit rusting of ferrous metal surfaces under static and dynamic conditions. As is to be expected, results will vary among specific materials used. In order to accomplish any given improvement, many of the additives can be used in relatively small amounts, as for dynamic rust prevention. If, on the other hand, it is desired to accomplish all the aforementioned beneficial results, this can be accomplished by use of relatively larger concentrations of the additive.

Over and above the aforesaid improvements imparted to distillate fuel 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, for 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 Example 23 showing preparation of a magnesium salt of a succinamic acid derived from a normal amine (Armeen 12D) which is a mixture of primary amines containing 2% decylamine, 95% dodecylamine and 3% tetradecylamine. 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 addition of the metal salt (Mg) of Example 2, the metal salt (Ba) of Example 3, and the metal salt (MG) of Example 23 in concentration of 50 lbs./thousand barrels of the fuel oil and the resulting compositions were subjected to the emulsion test described hereinafter.

Example 23

A mixture of 33⅓ gms. (⅓ mole) of succinic anhydride, 65 gms. (⅓ mole) of Armeen 12D and 205 gms. of xylene as diluent was heated at 95° C. for 2 hours with stirring to form the Armeen 12D succinamic acid. The Armeen 12D succinamic acid was then gradually added to 4 gms. (⅙ mole) of Mg in the form of a Mg methylate solution. The mixture was gradually heated to 130° C. to form the Mg salt. The Mg salt, being very viscous, was diluted with 103 gms. of isopropanol and filtered through Hyflo clay. The final product, the Mg salt of Armeed 12D succinamic acid, which contained 75% solvent (50% xylene+25% isopropanol), was clear and fluid at room temperature.

Analysis.—Estimated: Mg, 0.97%; N, 1.15%. Found: Mg, 1.2%; N, 1.29%.

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

Description of Emulsion

Rating

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

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

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

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

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

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

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

7 ____ Emulsion on bottom of water layer is almost solid. Emulsion on sides of bottles 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:

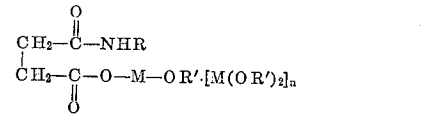
Base fuel:	Rating
Additive:	
Ex. 2	2
Ex. 3	2
Ex. 23	9

It is apparent from the foregoing that the metal salts of the succinamic acid derived from the tertiary-carbon atom amine effectively inhibited emulsification (Rating 2) whereas the corresponding metal salt (Ex. 23) but prepared from the normal amine resulted in a composition that emulsified severely.

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. A metal salt of the formula:



wherein R is a monovalent aliphatic hydrocarbon group having between 4 and 30 carbon atoms and a tertiary carbon atom linked to the nitrogen atom; R′ is a saturated aliphatic hydrocarbon group; M is a divalent metal; and *n* is an integer of 0 to 10.

2. A compound, as defined in claim 1, wherein R′ contains 1 to 18 carbon atoms, and *n* is an integer of 0 to 10.

3. A compound, as defined in claim 1, wherein R′ is methyl.

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