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3,039,860

N-SUBSTITUTED-ALKENYLSUCCINIMIDES IN DISTILLATE FUELS

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This invention 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 sediments during prolonged storage periods, to prevent screen-clogging, and to prevent rusting of ferrous metal surfaces, and with gasolines adapted to prevent rusting of ferrous metal surfaces.

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 and gasolines, 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 fuel is removed for transportation, sufficient water may be carried along to cause rusting of ferrous metal surfaces in pipelines, tankers, and the like.

It has now been found that the problems of sedimentation and screen clogging in fuel oils, and of rusting with gasolines and fuel oils can be solved by the use of a single addition agent. It has been discovered that distillate fuels containing minor amounts of certain succinimides and amine salts thereof are effectively inhibited, as aforesaid.

Accordingly, it is a broad object of this invention to provide fuels having properties improved with novel addition agents. Another object is to provide novel succinimides. A further object is to provide a fuel oil having an additive adapted to inhibit sedimentation, to prevent screen clogging, and to prevent rusting of ferrous metal surfaces with which it comes in contact. A still further object is to provide a gasoline containing an additive adapted to prevent rusting of ferrous metal surfaces with which the gasoline comes in contact. A specific object is to provide certain novel succinimides and amine salts thereof and distillate fuels containing them. 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 N-carboxymethylalkenyl-succinimides and N-(o-carboxyphenyl)-alkenyl-succinimides containing between about 8 carbon atoms and about 35 carbon atoms in the alkenyl group and the amine salts thereof with tertiary-alkyl primary amines having a tertiary carbon atom attached to the nitrogen atom and having between about 6 carbon atoms and about 30 carbon atoms per molecule; and distillate fuels containing at least one material from the group consisting of said succinimides and amine salts thereof.

The novel addition agents of this invention are N-carboxymethyl-alkenyl-succinimides and N-(o-carboxyphenyl)-alkenyl-succinimides; and amine salts thereof with tertiary-alkyl primary amines. The succinimides

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contemplated herein can be prepared by several methods known to the art for making cyclic imides. Most feasibly, they are prepared by reacting an alkenyl succinic acid anhydride or an alkenyl succinic acid with glycine (aminoacetic acid) or with anthranilic acid, in equimolar amounts and with the elimination of water of condensation. In the case of the anhydride, there will be formed one mole of water per mole of reactant, and with the acid, two moles of water are formed. Accordingly, the condensation will be carried out at temperatures of between about 150° C. and about 250° C., preferably between about 175° C. and about 200° C. The time of reaction will be dependent, of course, upon the reaction temperature employed. Reaction will continue until the required amount of water of condensation has evolved. Generally, the time will vary between about 2 hours and about 6 hours. Shorter reaction times are required if water is removed by azeotropic distillation. Suitable liquids which form azeotropes with water are non-polar solvents, such as benzene, toluene, xylenes, etc.

The alkenyl succinic acid anhydride reactant can have between 8 and 35 carbon atoms in the alkenyl radical, and preferably between 10 and 14 carbon atoms. Non-limiting examples of the alkenyl succinic acid anhydride reactants are octenyl succinic acid anhydride, diisobutyl succinic acid anhydride, 2-methylheptenyl succinic acid anhydride, 4-ethylhexenyl succinic acid anhydride, nonenyl succinic acid anhydride, decenyl succinic acid anhydride, undecenyl succinic acid anhydride, dodecenyl succinic acid anhydride, trisobutenyl succinic acid anhydride, tetrapropenyl succinic acid anhydride, tetradecenyl succinic acid anhydride, hexadecenyl succinic acid anhydride, 11-tricosenyl succinic anhydride, and 17-pentatriacontenyl succinic anhydride. As mentioned hereinbefore, the alkenyl succinic acids corresponding to these alkenyl succinic acid anhydrides can be used to prepare the compounds of this invention.

The amine salts of the N-carboxymethyl-alkenyl-succinimides and N-(o-carboxyphenyl)-alkenyl-succinimides of this invention are prepared readily by warming the succinimide with an equimolar amount of tertiary-alkyl primary amine. The addition takes place readily, without the elimination of water, but it is facilitated by heating to temperatures of between about 50° C. and about 100° C.

The amines utilizable in forming the salts of the N-carboxymethyl-alkenyl-succinimides and N-(o-carboxyphenyl)-alkenyl succinimides are the tertiary-alkyl, primary, monoamines in which a primary amino (—NH₂) group is attached to a tertiary carbon atom and which contain between about 6 carbon atoms and about 30 carbon atoms in the tertiary-alkyl radical; and mixtures thereof. These amines all contain the terminal group

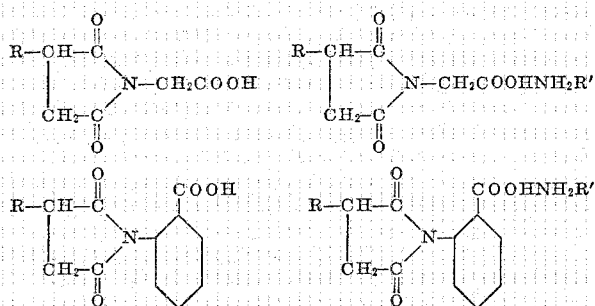


Non-limiting examples of the amine reactants are t-hexyl primary amine, t-octyl primary amine, t-nonyl primary amine, t-decyl primary amine, t-dodecyl primary amine, t-tetradecyl primary amine, t-octadecyl primary amine, t-eicosyl primary amine, t-docosyl primary amine, t-tetracosyl primary amine, and t-triacontyl primary amine. The amine reactants can be prepared in several ways well known to those skilled in the art. Specific methods of preparing the t-alkyl primary amines are disclosed in the Journal of Organic Chemistry, vol. 20, pages 295 et 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

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alkyl chloride with dry hydrogen chloride, and finally condensing the chloride with ammonia, under pressure, to produce a t-alkyl primary amine mixture.

The N-carboxymethyl-alkenyl-succinimides and N-(o-carboxyphenyl)-alkenyl-succinimides of this invention and the amine salts have the structures, respectively:



wherein R is an alkenyl group containing between 8 and 35 carbon atoms, preferably between 10 and 14 carbon atoms, and R' is a tertiary-alkyl radical containing between about 6 and about 30 carbon atoms.

The fuel oils that are improved in accordance with this invention are hydrocarbon fractions having an initial boiling point of at least about 100° F. and an end-boiling point no higher than about 750° F., and boiling substantially continuously throughout their distillation range. Such fuel oils are generally known as distillate fuel oils. It is to be understood, however, that this term is not restricted to straight-run distillate fractions. The distillate fuel oils can be straight-run distillate fuel oils, catalytically or thermally cracked (including hydrocracked) distillate fuel oils, or mixtures of straight-run distillate fuel oils, naphthas and the like, with cracked distillate stocks. Moreover, such fuel oils can be treated in accordance with well known commercial methods, such as, acid or caustic treatment, hydrogenation, solvent refining, clay treatment, etc.

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

Particularly, contemplated among the fuel oils are Nos. 1, 2, and 3 fuel oils used in heating and as diesel fuel oils, and the jet combustion fuels. The domestic fuel oils generally conform to the specifications set forth in ASTM 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 amount of N-carboxymethyl-alkenyl-succinimide, N-(o-carboxyphenyl)-alkenyl-succinimide or amine salt thereof that is added to distillate fuel in accordance with this invention will depend, of course, upon the intended purpose and the particular succinimide or salt selected, as they are not all equivalent in their activity. Some may

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have 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 in fuel oil, namely, to inhibit sedimentation, to reduce screen clogging, and to prevent rusting of ferrous metal surfaces, additive concentrations varying between about 10 pounds per thousand barrels of fuel (about 0.004 weight percent) and about 200 pounds per thousand barrels of oil (about 0.03 weight percent) 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 PPM, i.e., about one pound of additive per thousand barrels of oil (about 0.0004 weight percent), are effective. In gasoline the concentration of additive will vary between about 0.0004 percent and about 0.5 percent, by weight, of the gasoline. In preferred practice, amounts varying between about 0.005 percent and about 0.05 percent, by weight, are used. In general, therefore, the amount of succinimide of this invention or of amine salt thereof that can be added to the distillate fuel, in order to achieve a beneficial result, will vary generally 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 pounds and about 200 pounds per thousand barrels of fuel.

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 additives of the invention may be used in the gasoline along with other additives designed to impart other improved properties thereto. Thus, anti-knock agents, anti-stall additives, pre-ignition inhibitors, metal-deactivators, dyes, antioxidants, detergents, etc., may be present in the gasoline. Also, the gasoline may contain a small amount, from about 0.01 percent to about 1 percent, by weight, of a solvent oil or upperlube. Suitable oils, for example, include Coastal and Mid-Continent distillate oils having viscosities within the range of from about 50 to about 500 S.U.S. at 100° F. Synthetic oils, such as diester oils, polyalkylene glycols, silicones, phosphate esters, polypropylenes, polybutylenes and the like, may also be used.

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

AMIC ACIDS AND SALTS

The salt-forming amine reactant used in the specific working examples is a mixture 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 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.

Example 1

A mixture of 37.5 grams (0.5 mol) glycine and 150 grams (0.5 mol) tetrapropenyl succinic anhydride were

slowly heated to a temperature of about 200° C. over a period of about 12 hours. Nine grams (0.5 mol) of water were evolved during the course of the reaction.

Example 2

A mixture of 37.5 grams (0.5 mol) glycine and 150 grams (0.5 mol) tetrapropenyl succinic anhydride were slowly heated to a temperature of about 200° C. over a period of about 12 hours. The mixture was cooled to about 75° C. and 100 grams (0.5 mol) of Amine A was added. The mixture was stirred for about 2 hours at 100° C. to insure complete reaction.

Example 3

A mixture of 75 grams (0.55 mol) anthranilic acid and 150 grams (0.55 mol) tetrapropenyl succinic anhydride were slowly heated to a temperature of about 200° C. over a period of about 12 hours. Ten grams (0.55 mol) of water were evolved during the course of the reaction.

SEDIMENTATION

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

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 I. The test fuel oil was a blend of 80 percent distillate stock obtained from continuous catalytic cracking and 20 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

110° F. STORAGE TEST—12 WEEKS

Additive of Example	Conc'n., lbs./1,000 bbls.	Sediment, mg./liter
Blank.....		12
1.....	25	10
2.....	25	3
3.....	25	9

SCREEN CLOGGING

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

Blends were prepared in the aforescribed test fuel oil and subjected to the Screen Clogging Test. Results are set forth in Table II.

Table II

SCREEN CLOGGING

Additive of Example	Conc'n., lbs./1,000 bbls.	Screen Clogging, Percent
Blank.....		100
1.....	25	2
2.....	25	12

RUSTING

The method used for testing anti-rust properties of gasolines 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 to prevent rusting of ferrous metal surfaces in pipelines, tubes, etc.

Blends of the additives described in the examples in the test gasoline were subjected to the ASTM Rust Test D-665. This test gasoline was a blend of 80 volume percent catalytically cracked gasoline and 20 volume percent straight-run gasoline, which had a boiling range of 100° F. to 400° F. Pertinent data are set forth in Table III.

Table III

ASTM RUST TEST D-665

Additive of Example	Conc'n., parts per million	Rust Test Result
Blank.....		Fail.
1.....	5	Pass.
2.....	5	Do.
3.....	25	Do.

The Static Rust Test simulates conditions encountered in storage tanks, such as, the home fuel oil storage tank. In this test, a strip of 16-20 gauge sand blasted steel plate is placed in a clear quart bottle. The length of the strip is sufficient to reach from the bottom of the bottle into the neck of the bottle without interfering with the cap. One hundred cc. of synthetic sea water with pH adjusted to 5 (ASTM D-665) and 750 cc. of test oil are placed in the bottle. The bottle is capped tightly, shaken vigorously for one minute, and permitted to stand quietly at 80° F. for 21 days. At the end of that time, the amount of rust that occurs on the surface of the plate immersed in the water is used as a measure of effectiveness of the fuel to inhibit rusting in storage vessels. It is generally preferred that no more than 5 percent of the surface should be rusted. This test is much more severe than the ASTM Rust Test. Many additive compositions that pass the ASTM test fail in the Static Test. On the other hand, materials that pass the Static Test always pass the ASTM test.

Blends of additives in the aforescribed test fuel oil were subjected to the Static Rust Test. Pertinent results are set forth in Table IV.

Table IV

STATIC RUST TEST

Additive of Example	Conc'n., lbs./1,000 bbls.	Percent Rusting
Blank.....		100
1.....	25	0
2.....	25	0

It will be apparent, from the data set forth in Tables I through IV, that the succinimides and salts of this invention, are highly effective to reduce sedimentation and screen clogging and to inhibit rusting of ferrous metal

surfaces. 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 at the practical additive concentration of 50-100 pounds per thousand barrels of fuel oil.

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 petroleum distillate fuel containing between about one pound per thousand barrels of fuel and about 200 pounds per thousand barrels of fuel of at least one material selected from the group consisting of (1) N-carboxymethyl-alkenyl-succinimides, containing between about 8 carbon atoms and about 35 carbon atoms in the alkenyl group thereof, (2) N-(o-carboxyphenyl)-alkenyl-succinimides containing between about 8 carbon atoms and about 35 carbon atoms in the alkenyl group thereof, and (3) amine salts of (1) and (2) with tertiary-alkyl primary amines having a tertiary carbon atom attached to the nitrogen atom and having between about 6 carbon atoms and about 30 carbon atoms per molecule.

2. A distillate fuel oil containing between about 10 pounds per thousand barrels of fuel oil and about 200 pounds per thousand barrels of fuel oil of at least one material selected from the group consisting of (1) N-carboxymethyl-alkenyl-succinimides, containing between about 8 carbon atoms and about 35 carbon atoms in the alkenyl group thereof, (2) N-(o-carboxyphenyl)-alkenyl-succinimides containing between about 8 carbon atoms and about 35 carbon atoms in the alkenyl group thereof, and (3) amine salts of (1) and (2) with tertiary-alkyl primary amines having a tertiary carbon atom attached to the nitrogen atom and having between about 6 carbon atoms and about 30 carbon atoms per molecule.

3. A gasoline containing between about 0.0004 percent and about 0.5 percent, by weight of the gasoline of at least one material selected from the group consisting of (1) N-carboxymethyl-alkenyl-succinimides containing between about 8 carbon atoms and about 35 carbon atoms in the alkenyl group thereof, (2) N-(o-carboxyphenyl)-alkenyl-succinimides containing between about 8

carbon atoms and about 35 carbon atoms in the alkenyl group thereof, and (3) amine salts of (1) and (2) with tertiary-alkyl primary amines having a tertiary carbon atom attached to the nitrogen atom and having between about 6 carbon atoms and about 30 carbon atoms per molecule.

4. A distillate fuel oil containing between about 10 pounds per thousand barrels of fuel oil and about 200 pounds per thousand barrels of fuel oil of N-carboxymethyl-tetrapropenyl-succinimide.

5. A distillate fuel oil containing between about 10 pounds per thousand barrels of fuel oil and about 200 pounds per thousand barrels of fuel oil of an amine salt of N-carboxymethyl-tetrapropenyl-succinimide, wherein the salt-forming amine is a mixture of primary amines having a tertiary carbon atom attached to the amino group and containing 12 to 15 carbon atoms per amine molecule and averaging 12 carbon atoms per molecule.

6. A distillate fuel oil containing between about 10 pounds per thousand barrels of fuel oil and about 200 pounds per thousand barrels of fuel oil of N-(o-carboxyphenyl)-tetrapropenyl-succinimide.

7. A gasoline containing between about 0.0004 percent and about 0.5 percent, by weight of the gasoline, of N-carboxymethyl-tetrapropenyl-succinimide.

8. A gasoline containing between about 0.0004 percent and about 0.5 percent, by weight of the gasoline, of an amine salt of N-carboxymethyl-tetrapropenyl-succinimide, wherein the salt-forming amine is a mixture of primary amines having a tertiary carbon atom attached to the amino group and containing 12 to 15 carbon atoms per amine molecule and averaging 12 carbon atoms per molecule.

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