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3,095,286

## STABILIZED DISTILLATE FUEL OIL

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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 sediment during prolonged storage periods, to prevent screen-clogging, and 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, 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 aforescribed 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 compatibility, 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 been proposed to overcome two difficulties, e.g., sedimentation and screen clogging, with one additive. Insofar as is known, however, no single addition agent has been found effective against sedimentation, screen and nozzle clogging, and rusting of ferrous metal surfaces.

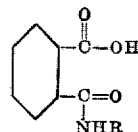
It has now been found that all three problems, i.e., sedimentation, screen clogging, and rusting, can be solved by the use of a single fuel oil addition agent. It has been discovered that a distillate fuel oil containing minor amounts of certain amic acids and amine salts thereof is effectively inhibited, simultaneously, against all three aforementioned difficulties.

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 that contains certain amic acids or amine salts thereof that achieve these results. Other objects and advantages of this invention will become apparent to those skilled in the art from the following detailed description.

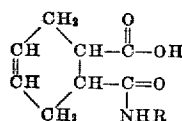
The present invention provides a distillate fuel oil containing a minor amount, sufficient to inhibit sedimentation and screen clogging and to prevent rusting of ferrous metal surfaces in contact therewith, of a com-

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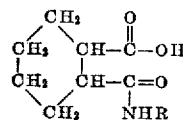
pound selected from the group consisting of (1) a phthalamic acid having the formula:



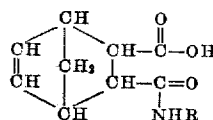
wherein R is a monovalent aliphatic hydrocarbon radical having between about 4 and about 30 carbon atoms; (2) a tetrahydrophthalamic acid having the formula:



wherein R is a monovalent aliphatic hydrocarbon radical having between about 4 and about 30 carbon atoms; (3) a hexahydrophthalamic acid having the formula:

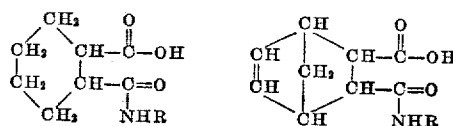
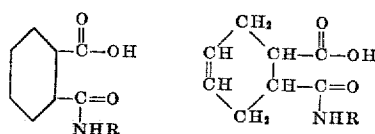


wherein R is a monovalent aliphatic hydrocarbon radical having between about 4 and about 30 carbon atoms; (4) a nadamic acid having the formula:



wherein R is a monovalent aliphatic hydrocarbon radical having between about 4 and about 30 carbon atoms; and (5) the salts of (1), (2), (3), and (4) with aliphatic primary amines having between about 4 and about 30 carbon atoms per molecule.

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



wherein R, in each case, is an aliphatic hydrocarbon radical of an aliphatic primary amine having between about 4 and about 30 carbon atoms per radical, and the amine salt of these amic acids with an aliphatic primary amine having between about 4 and about 30 carbon atoms per molecule. 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 equimolar amounts of phthalic acid anhydride, tetrahydrophthalic acid anhydride, hexahydrophthalic acid anhydride, or nadic acid anhydride, respectively, and an aliphatic primary 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 three hours. The addition occurs readily without the formation of water. Less de-

sirably, the amic acids can be prepared by the controlled reaction between phthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, or nadic acid and the amine, with the elimination of one mole of water per mole of amic acid produced. Care must be exercised, however, to avoid the elimination of two moles of water to form the cyclic imide. Regardless of the method used to form the amic acid, the salt thereof can be made readily by warming equimolar quantities of the amic acid and an aliphatic primary amine having between about 4 and about 30 carbon atoms per molecule. The salt-forming amine can be the same amine used in making the amic acid, or it can be a different amine. In the case where the salt-forming amine is the same used in the amic acid, the salt can be made by heating two moles of amine with one mole of acid anhydride under temperatures whereby water is not evolved.

The amines utilizable in forming the amic acids and the salts thereof are the primary aliphatic amines having between about 4 and about 30 carbon atoms per molecule. These are the monoamines having a single open chain hydrocarbon group attached to a nitrogen atom. The aliphatic radical can be saturated or unsaturated, and branched-chain or normal chain. Likewise mixtures of these amines, as well as pure amines, can be employed. A very useful and readily available class of primary amines are the tertiary-alkyl, primary, monoamines in which a primary amino ( $-\text{NH}_2$ ) 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 amine, n-butyl amine, t-hexyl primary amine, n-hexylamine, n-octylamine, n-octenylamine, t-octyl primary amine, 2-ethylhexylamine, t-decyl primary amine, n-decylamine, t-dodecyl primary amine, n-undecylamine, dodecylamine, dodecadienylamine, tetradecylamine, t-tetradecyl primary amine, t-octadecyl primary amine, hexadecylamine, octadecylamine, octadecadienyl 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, page 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 alkyl chloride with dry hydrogen chloride, and finally condensing the chloride with ammonia, under pressure, to produce a t-alkyl primary amine mixture.

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

The distillate fuel oils are characterized by their relatively low viscosities, pour points, and the like. The principal property which characterizes the contemplated hydrocarbons, however, is the distillation range. As

mentioned hereinbefore, this range will lie between about 100° F. and about 750° F. Obviously, the distillation range of each individual fuel oil will cover a narrower boiling range falling, nevertheless, within the above-specified limits. Likewise, each fuel oil will boil substantially continuously throughout its distillation range.

Particularly contemplated among the fuel oils are Nos. 1, 2, and 3 fuel oils used in heating and as diesel fuel oils, and the jet combustion fuels. The domestic fuel oils generally conform to the specifications set forth in ASTM Specifications D396-48T. Specifications for diesel fuels are defined in ASTM Specifications D975-48T. Typical jet fuels are defined in Military Specification MIL-F-5624B.

The amount of phthalamic acid or amine salt of phthalamic acid additives that is added to the distillate fuel oil in accordance with this invention will depend, of course, upon the intended purpose and the particular amic acid or salt selected, as they are not all equivalent in their activity. Some may have to be used in greater concentrations than others to be effective. In most cases, in which it is desired to obtain all 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 amic acid or of amine 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 pounds 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 acids or amine salts thereof and fuel oils, as discussed hereinbefore, can be used, as those skilled in the art will readily appreciate.

#### AMIC ACIDS AND SALTS

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 ( $-\text{NH}_2$ ) 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.

"Amine B" is a mixture of normal aliphatic primary amines containing, by weight, 10 percent hexadecyl amine, 10 percent octadecyl amine, 35 percent octadecenyl amine, and 45 percent octadecadienyl amine.

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**Example 1**

A mixture of 100 grams (0.5 mole) of Amine A, 74 grams (0.5 mole) of phthalic acid anhydride, and 90 grams xylene, as a diluent, was heated with stirring at 65° C. for 3 hours to form the Amine A phthalamic acid.

**Example 2**

A mixture of 150 grams (0.5 mole) of Amine B and 74 grams (0.5 mole) of phthalic acid anhydride was heated at 80–85° C. with stirring for 3 hours to form the Amine B phthalamic acid.

**Example 3**

A mixture of 50 grams (1/2 mole) of Amine B, 24.7 grams (1/2 mole) of phthalic acid anhydride, and 125 grams of xylene diluent was stirred at 75° C. for 1.5 hours to form the Amine B phthalamic acid. At room temperature 50 grams (1/2 mole) of Amine B was added to this amic acid. The mixture was heated with stirring at 75–80° C. for 1.5 hours to form the Amine B salt of the Amine B phthalamic acid.

**Example 4**

This run illustrates the preparation of the amic acid salt in one step. A mixture of 150 grams (0.5 mole) of Amine B, 37 grams (0.25 mole) of phthalic acid anhydride, and 100 grams toluene, as a diluent, was stirred at 90° C. for 6 hours to form the Amine B salt of the Amine B phthalamic acid.

**Example 5**

A mixture of 100 grams (0.5 mole) of Amine A, 76 grams (0.5 mole) of tetrahydrophthalic anhydride and 176 grams of xylene diluent was stirred at 100° C. for three hours to form the tetrahydrophthalamic acid.

**Example 6**

A mixture of 100 grams (0.5 mole) of Amine A, 77 grams (0.5 mole) of hexahydrophthalic anhydride and 177 grams of xylene diluent was stirred at 100° C. for three hours to form the hexahydrophthalamic acid.

**Example 7**

A mixture of 100 grams (0.5 mole) of Amine A, 82 grams (0.5 mole) of nadic anhydride and 182 grams of xylene diluent was stirred at 100° C. for three hours to form the nadic amic acid.

**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 convection 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 sedimentation. 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 8**

The additives described in Examples 1, 3, and 4 were blended in a 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 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.

Similarly, the additives described in Examples 5, 6, and 7 were blended in a test fuel oil and subjected to the storage test. Results are set forth in Table I. The test fuel

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in this case, was the fuel described in the preceding paragraph that had been hydrodesulfurized.

TABLE I.—110° F. STORAGE TEST—12 WEEKS

Example	Inhibitor			Inhibitor Conc'n, lb./1,000 bbls.	Sediment, mg./liter
	Acid Anhydride	Amic Amine <sup>1</sup>	Salt Amine <sup>2</sup>		
1	(blank)	A		0	24
	(Phthalic)			25	13
3	(blank)	B	B	0	150
	(Phthalic)			100	140
4	(blank)	B	B	0	25
	(Phthalic)			100	13
5	(blank)	A		0	5
	(Tetrahydrophthalic)			25	3
6	(blank)	A		0	5
	(Hexahydrophthalic)			25	2
7	(blank)	A		0	5
	(Nadic)			25	2

<sup>1</sup>Amine combined with anhydride to form the amic acid.

<sup>2</sup>Amine used to form salt of the amic acid.

**SCREEN CLOGGING**

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

**Example 9**

Using the test fuel oil described in the first paragraph of Example 8, blends of the additives of Examples 2, 3, 5, 6, and 7 in this fuel were prepared. Each blend was subjected to the screen clogging test, as aforescribed. 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	0	100
2	100	14
3	100	14
5	25	16
6	50	54
7	25	27

**RUSTING**

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

**Example 10**

Blends of the additives described in Examples 1, 2, and 3 in the fuel oil of Example 9 were subjected to the ASTM Rust Test D-665. Pertinent data are set forth in Table III.

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TABLE III.—ASTM RUST TEST

Additive of Example	Conc'n, p.p.m.	Test Result
Blank.....	0	Fail.
2.....	10	Pass.
3.....	10	Pass.

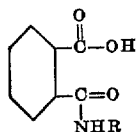
It will be apparent, from the data set forth in Tables I through III, that the amic acids of this invention and amine salts thereof are highly effective to reduce sedimentation and screen clogging and to inhibit rusting of ferrous metal surfaces. As it is to be expected results will vary among specific 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:

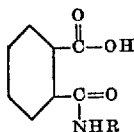
1. As a new liquid composition, a petroleum distillate fuel oil having an initial boiling point of at least about 100° F. and an end boiling point no higher than about 750° F. containing between about one pound and about 200 pounds, per thousand barrels of fuel and sufficient to inhibit said fuel oil against screen clogging and sedimentation, of a compound from the group consisting of

(1) a phthalamic acid having the formula:



wherein R is a mixture of aliphatic hydrocarbon radicals having between about 12 and about 18 carbon atoms and (2) salts of said phthalamic acid with an aliphatic primary amine having between about 4 and about 30 carbon atoms per molecule.

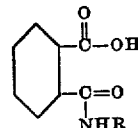
2. As a new liquid composition, a distillate fuel oil having an initial boiling point of at least about 100° F. and an end point no higher than about 750° F.; containing between about 10 pounds and about 200 pounds, per thousand barrels of fuel and sufficient to inhibit said fuel oil against screen clogging and sedimentation, of a phthalamic acid having the formula:



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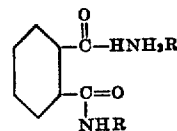
wherein R is a mixture of alkyl radicals having a tertiary carbon atom attached to the nitrogen atom, said mixture being about 85 weight percent tertiary dodecyl, about 10 weight percent tertiary pentadecyl, and less than 5 weight percent tertiary alkyl radicals having less than 12 and more than 15 carbon atoms.

3. As a new liquid composition, a distillate fuel oil having an initial boiling point of at least about 100° F. and an end boiling point no higher than about 750° F. containing between about one pound and about 200 pounds, per thousand barrels of fuel and sufficient to inhibit said fuel oil against screen clogging and sedimentation, of a phthalamic acid having the formula:



wherein R is a mixture of normal aliphatic radicals containing, by weight, about 10 percent hexadecyl, about 10 percent octadecyl, about 35 percent octadecenyl, and about 45 percent octadecadienyl.

4. As a new liquid composition, a distillate fuel oil having an initial boiling point of at least about 100° F. and an end boiling point no higher than about 750° F. containing between about one pound and about 200 pounds, per thousand barrels of fuel and sufficient to inhibit said fuel oil against screen clogging and sedimentation, of an amine salt of a phthalamic acid having the formula:



wherein R is a mixture of normal aliphatic radicals containing, by weight, about 10 percent hexadecyl, about 10 percent octadecyl, about 35 percent octadecenyl, and about 45 percent octadecadienyl.

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