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FUEL OIL COMPOSITION

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15 Claims. (Cl. 44—63)

This invention has to do with improved fuel oil compositions. More specifically it has to do with fuel oils which have been stabilized and which are particularly suitable for use as industrial and domestic fuels.

This application is a continuation-in-part of my application Serial No. 661,291, filed May 24, 1957, which, in turn, is a continuation-in-part of my earlier application Serial No. 596,460, filed July 9, 1956. The two applications have been abandoned.

The fuel oils improved in accordance with this invention are hydrocarbon fractions having initial boiling points of at least about 100° F. and end points not higher than about 750° F., and which boil substantially continuously throughout their distillation ranges. 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. Thus, as is well known to those skilled in the art, the distillate fuel oils can be straight-run distillate fuel oils, catalytically or thermally cracked distillate fuel oils or mixtures of straight-run distillates, 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, 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 hydrocarbon fractions, 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 range falling, nevertheless, within the above-specified limits. Likewise, each fuel oil will boil substantially, continuously throughout its distillation range.

The fuel oils particularly contemplated herein are Nos. 1, 2 and 3 fuel oils used in domestic heating and as diesel fuel oils, particularly those made up chiefly or entirely of cracked distillate stocks. The domestic heating oils generally conform to the specification set forth in ASTM Specifications D396–48T; the boiling characteristics are such as the following: ten (10) percent evaporation at a maximum temperature of 350° F.–440° F.; ninety (90) percent evaporation at a maximum temperature ranging from 450 to 675° F. The specifications for diesel fuels are defined as ASTM Specifications D975–48T; the boiling characteristics are illustrated by: ninety (90) percent evaporation at a maximum temperature varying from about 550° F. to about 675° F. and an end point varying from about 575° F. to about 725° F.

Contemplated herein also are fuels for jet combustion engines, also referred to as aviation turbines. Typical jet fuels are defined in Military Specification MIL–F–5624B. For example, such fuels can have: a ninitial boiling point of 250° F., a ten (10) percent evaporation at 410° F., fifty (50) percent at 425° F., ninety (90) percent at 500° F., and end point of 572° F. In general, jet fuels contain hydrocarbons boiling in the gasoline and fuel oil ranges, with the major proportion being in the latter range.

In recent years, fuel oils of the foregoing character have been subjected to relatively mild hydrogenation treatments in order to improve them in one or more properties. Sulfur-content is generally reduced, so too is phenol and nitrogen contents. Typical of such mild hydrogenation treatments, generally designated in the art as "hydrofining" of fuels, is that described by H. Hoog in U.S. Patent No. 2,608,521, issued August 26, 1952. Advantageous mild hydrogenation procedures are described by F. J. Ciapetta et al. in Serial No. 360,662, filed June 10, 1953. By way of illustration, a fuel oil can be mildly hydrogenated in the presence of a cobalt molybdate catalyst under conditions including: a temperature of 600–750° F.; hydrogen pressure of 200–1000 pounds per square inch; hydrogen recycle of 1000 cubic feet per barrel of oil; hydrogen consumption of 50–250 cubic feet per barrel of oil.

As is well known in the art, fuel oils of the above-defined character have a tendency to deteriorate in storage and to form colored bodies and sludge therein. It is to be recognized that such undesirable features are less pronounced with hydrofined fuel oils than with fuel oils not so treated; however, hydrofined oils are less responsive to agents added to reduce sediment formation and/or screen-clogging, and other agents added to inhibit rust formation. This deterioration of the oil is highly undesirable in that it causes serious adverse effects on the characteristics of the oil, particularly on the ignition and burning qualities thereof. It is also a contributory factor, along with the presence of other impurities in the oil, such as rust, dirt and moisture, in causing clogging of the equipment parts, such as screens, filters, nozzles, etc., as is explained hereinbelow. An important economical factor is also involved in the problem of oil deterioration in storage, viz., customer resistance. Thus, customers judge the quality of an oil by its color and they oftentimes refuse to purchase highly colored oils. It will be appreciated, then, that since fuel oils of necessity are generally subject to considerable periods of storage prior to use, the provision of a practical means for preventing the deterioration of the fuel oil during such storage would be a highly desirable and important contribution to the art.

Another and distinct problem that has plagued fuel oil manufacturers and users is that referred to as "screen-clogging." This involves the deposition of foreign substances, such as water droplets, rust and dirt particles, as well as any sludge material formed by the deterioration of the oil, on the metallic surfaces of screens and filters of burners and engines in which the oil is utilized. Additives have been developed to impart anti-clogging properties to fuel oils, functioning therein to inhibit the aforesaid deposition of foreign substances. The mechanism by which the clogging is prevented involves the adsorption of the anti-clogging agent or additive on the metal surfaces whereby the contacting of these surfaces by the foreign substances and/or preformed sludge is prevented. In this way, deposition and build-up of these materials on the metal surfaces is avoided. It will be appreciated, therefore, that the problem of preventing screen-clogging by fuel oils is entirely different from that of preventing the formation of sediment and color therein as occurs in the oil during prolonged periods of storage. Thus, it will be appreciated that any fuel distribution system will contain small amounts of foreign substances, such as condensed moisture and particles of rust and dirt, which become entrained in the oil, even though the oil has not been stored for any appreciable length of time. On the other hand, fuel oils which have been in storage for substantial periods of time will also contain another kind of sediment, or sludge, which is produced by the gradual deterioration of the oil per se. This sediment, or sludge, is formed in the oil as the result of chemical phenomena. Thus, during storage, oxidation of the various components of the oil, such as pyrrolic compounds; phenols and thiophenols present therein, takes place forming quinoid molecules which condense with one another and/or with other active hydrogen compounds also present in the oil to

produce highly colored bodies of increasing molecular weight. When an oil has been in storage for any substantial period of time these compounds separate out as insoluble sludge. Additives have also been developed to inhibit the formation of sediment or sludge in the oil due to oxidative deterioration of the oil in storage, as above described. Such additives act by inhibiting the initial oxidation and the subsequent reactions which produce such sludge.

It is apparent, then, that the problem of preventing screen-clogging by fuel oils is entirely different from the problem of preventing the formation of sediment and color therein as occurs in the oil during prolonged periods of storage. As evidence of the difference between these problems, additives which prevent screen-clogging will not necessarily have any effectiveness in preventing the formation of sediment and color. Correspondingly, other additives which effectively inhibit sediment and color formation do not necessarily have anti-screen clogging properties.

Another serious problem encountered with fuel oils is their tendency to emulsify when in contact with relatively small amounts of water. During storage and transportation of fuel oils, water often gets into storage tanks, pipelines, tankers, and like storage equipment. Then, when the fuel oils are to be used, equipment difficulties and/or ignition failure result from the emulsions formed of the fuel and water. This problem becomes more severe when certain additives are present in the oils, the additives serving to improve the oils in one or more properties but serving to increase the emulsification tendencies of the oils. This is demonstrated hereinafter by representative test results.

It is the object of this invention to stabilize fuel oils.

It is a further object of the invention to provide fuel oils stabilized against the formation of sediment therein.

Still another object of the invention is to provide a fuel oil free from screen-clogging tendencies.

An important object of the invention is to provide a fuel oil stabilized against the formation of sediment and color and also free from screen-clogging tendencies.

A still further object of the invention is to provide a fuel oil having excellent anti-rust properties.

A primary object of the invention is to provide a fuel oil improved as indicated by the foregoing objects and further improved by having little or no tendency to emulsify when in contact with small amounts of water.

Additional objects of the invention will be apparent from the following description:

It has been discovered that the aforesaid objects are realized by incorporating in a fuel oil of the character described above, a small amount of a fuel-oil-soluble reaction product obtained by reacting a naphthenic acid, having a molecular weight up to about 300, with an alkylene polyamine represented by the general formula:



wherein: R is an alkylene group having either 2 or 3 carbon atoms; R′ is hydrogen or an aliphatic group preferably an aliphatic group having from about 8 to about 18 carbon atoms; and *n* is an integer of at least 2 and preferably 2 to 4 when R has 2 carbon atoms, and *n* is an integer of at least 1 and preferably 2 to 4 when R has 3 carbon atoms, there being no upper limit to the number of alkylene groups in the molecule.

As indicated by the foregoing general formula, the aliphatic polyamines contemplated herein include polyethylene polyamines. Typical of such compounds are diethylene triamine, triethylene tetramine, tetraethylene pentamine and pentaethylene hexamine. Of such polyamines, it has been found that diethylene triamine is particularly advantageous herein and represents a preferred reactant.

Included also among the polyamines of the foregoing general formula are propylene polyamines. Of such polyamines, preferred are those characterized by one primary amino group and one secondary amino group, the said amino groups being linked to different terminal carbon atoms of a normal propyl group. Representative of such amines are propylene diamine and iminobis propyl amine (i.e., dipropylene triamine).

Particularly outstanding of the propylene diamines are N-substituted propylene diamines wherein the substituent group contains from about 8 to about 18 carbon atoms. A number of mixtures of such diamines are presently available commercially. The diamines of the mixtures are represented structurally by $R'NHCH_2CH_2CH_2NH_2$ wherein R′ is aliphatic in nature, and varies from about 8 to about 18 carbon atoms. One such mixture, identified herein as "A," is one wherein about 10% of the R′ groups are hexadecyl, about 10% are octadecyl, about 35% are octadecenyl, and about 45% are octadecadienyl. Another mixture is "B"; in this product about 8% of the R′ groups are octyl, about 9% are decyl, about 47% are dodecyl, about 18% are tetradecyl, about 8% are hexadecyl, about 5% are octadecyl and about 5% are octadecenyl. A third mixture is "C," in which about 30% of the R′ group are hexadecyl, about 25% are octadecyl and about 45% are octadecenyl. Of such mixtures, mixture "A" is particularly preferred herein.

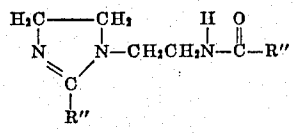
Reacted with the polyamines described above are naphthenic acids which are monocarboxylic acids obtained from crude petroleum or from distillates thereof. Such acids are well known in the art, having been well described in the Encyclopedia of Chemical Technology, edited by R. F. Kirk et al.; The Interscience Encyclopedia, Inc., New York, 1952, volume 9, pages 241–247; and by Carleton Ellis in "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., Inc.; New York, 1934; chapter 48. Earlier it had been considered that all naphthenic acids could be used for reaction with the aforementioned alkylene polyamines to form satisfactory products. However, it has been discovered that only certain naphthenic acids are suitable. The naphthenic acids which form reaction products capable of inhibiting emulsion formation in a fuel oil, are those having molecular weights up to about 300. This corresponds to an acid number above about 180, and an average of up to about 19 carbon atoms per molecule. Excellent results have been obtained with a naphthenic acid having an acid number of about 200, an average molecular weight of 275–300, and a major proportion thereof having from 15 to 19 carbon atoms per molecule. Naphthenic acids available commercially to date are mixtures rather than individual compounds.

The reaction products of this invention are prepared by reaction of from about 2 to about 4 molar proportions of a naphthenic acid with one molar proportion of an alkylene polyamine of the character described above wherein R′ is hydrogen or is an aliphatic group having less than about 7 carbon atoms; a preferred ratio is 2:1. Contemplated herein also are reaction products obtained by reaction of from about 1 to about 2 molar proportions of a naphthenic acid with one molar proportion of of an alkylene polyamine represented by the general formula, wherein R′ has at least about 8 carbon atoms; the preferred ratio for preparing such products is 1:1.

Products formed by reacting one molar proportion of a naphthenic acid with one molar proportion of an alkylene polyamine wherein R′ is hydrogen or an aliphatic group of about 7 carbons or less, are not completely soluble in fuel oil and do not act as sediment inhibitors therein. Products prepared by reacting more than two molar proportions of naphthenic acid with one molar proportion of an alkylene polyamine having an R′ group of hydrogen or an aliphatic group of about C_7 or less, are less effective sediment inhibitors and anti-screen-clog-

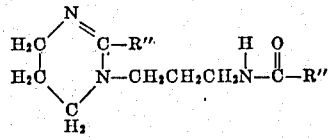
ging agents, than are those products obtained by using a molar ratio of 2:1. Products prepared by reacting more than one molar proportion of naphthenic acid with one molar proportion of an alkylene polyamine having an R' group of C_8 or greater, are likewise less effective than are those products obtained by using a molar ratio of 1:1.

When the alkylene polyamine used is a polyethylene polyamine such as diethylene triamine, and two molar proportions of a naphthenic acid are reacted with one molar proportion of said amine, the reaction product so obtained, most probably, is predominantly comprised of one or more imidazolines represented by the general formula:



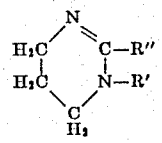
wherein R'' is naphthenyl.

When the alkylene polyamine is a polypropylene polyamine such as dipropylene triamine, and two molar proportions of naphthenic acid are reacted with one molar proportion of the amine, the reaction product so obtained, most probably, is predominantly comprised of one or more tetrahydropyrimidines represented by the general formula:



wherein R'' is naphthenyl.

Correspondingly, when the alkylene polyamine used is a propylene polyamine such as an N-octyl propylene diamine, and one molar proportion of naphthenic acid is reacted with one molar proportion of said diamine, the reaction product is considered to be primarily comprised of one or more tetrahydropyrimidines of the following formula:



wherein R' is octyl and R'' is naphthenyl.

It will be clear, therefore, that since available naphthenic acids are mixtures, since some of the polyamines are mixtures, and since the molar ratios of the naphthenic acid and polyamines are subject to some variations, the products are better described as reaction products than as individual compounds. This is particularly so when mixtures of diamines, such as "A," "B" and "C" above, are used as reactants.

The reaction products contemplated herein are used in fuel oils in concentrations varying between about 1 pound per thousand barrels of oil, and about 200 pounds per thousand barrels of oil. Preferably the concentration will vary between about 10 and 100 pounds per thousand barrels. In terms of weight percent, based upon the weight of the fuel oil, the concentrations vary preferably between about 0.005% and about 0.05%.

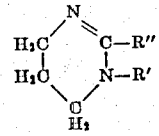
If it is desired, the fuel oil compositions of this invention can contain other additives for the purpose of achieving other results. Thus, for example, there can be present foam inhibitors, anti-rust agents, and ignition and burning quality improving agents. Examples of such additives are silicones, dinitropropane, amylnitrate, metal sulfonates and the like. A further example of other additives which may be used with the new fuel oil compositions are tertiary alkyl primary amines described in application Serial No. 578,881, filed April 18, 1956, now Patent No. 2,947,749.

The following specific examples are set forth for the purpose of illustrating the fuel oil compositions of this invention and for the purpose of distinguishing them from related fuel oil compositions. In such examples, the reaction products formed from naphthenic acids illustrate the invention.

TETRAHYDROPYRIMIDINE-CONTAINING REACTION PRODUCTS

Example 1

The following preparation illustrates a typical method for producing a reaction product containing tetrahydropyrimidines. A mixture of 1 mole (282 parts by weight) of oleic acid and 1 mole (370 parts) of amine mixture "A," described above, was refluxed in xylene solution for 4 hours. The reaction mixture was then slowly heated to 235° C. and was held at this temperature until the evolution of water ceased. Two (2) moles (36 parts) of water were collected. The final product, containing 4.0 percent of nitrogen, is a mixture of 2,3-disubstituted tetrahydropyrimidines which corresponds to the formula:



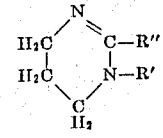
where R''=heptadecenyl and R'=10% octadecyl, 10% hexadecyl, 35% octadecenyl, and 45% octadecadienyl.

Example 2

A mixture of 1.15 moles (350 parts) of a commercial tall oil (identified herein as mixture "D") and 1.15 moles (330 parts) of amine mixture "B," identified above, was refluxed in xylene solution for 4 hours. The reaction mixture was then heated to 240° C. during a period of 6 hours. About 2.1 moles (38 parts) of water were collected.

Mixture "D" is a refined tall oil having an acid number of 185 and comprising a mixture of rosin acids and fatty acids. The fatty acids range from C_{16} to C_{18}.

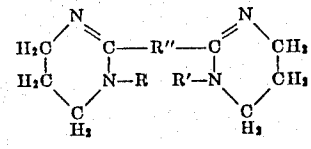
The final product, containing 2.86 percent nitrogen, is a mixture of a 2,3-disubstituted tetrahydropyrimidines corresponding to the formula:



where R''=alkyl groups from tall oil (a mixture of rosin and fatty acids) and R'=a mixture of C_8 to C_{18} alkyl groups and averaging C_{12} in molecular weight.

Example 3

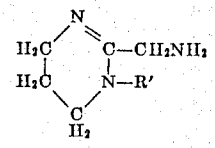
A mixture of 0.28 mole (100 parts) of a crude mixture of dimer acids (identified herein as mixture "E") and 0.56 mole (200 parts) of amine mixture "C," described above, was refluxed in xylene solution for 4 hours. The reaction mixture was then heated to 220° C. during a period of 10 hours. One mole (18 parts) of water was collected. The crude mixture of dimer acids has an acid number of 155 and comprises acids ranging from C_{32}–C_{54}. The final product, containing 4.8 percent of nitrogen, is a mixture of bis 2-(3 alkyl tetrahydropyrimydyl) alkylene corresponding to the formula:



where R''=alkenyl group from dimer acids and R'=a mixture of 30% hexadecyl, 25% octadecyl and 45% octadecenyl.

Example 4

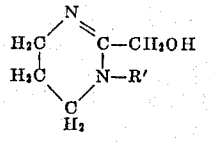
A mixture of 0.25 mole (19 parts) of glycine and 0.25 mole (93 parts) of amine mixture "A" was refluxed in xylene slurry for 4 hours. The reaction mixture was then heated to 225° C. during a period of 4 hours. About 0.55 mole (10 parts) of water was collected. The final product, containing 9.5 percent of nitrogen, is a mixture of 2-amino-methyl, 3-alkyl substituted tetrahydropyrimidines corresponding to the formula:



where R'=10% hexadecyl, 10% octadecyl, 35% octadecenyl and 45% octadecadienyl.

Example 5

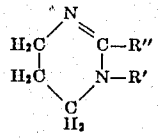
A mixture of 0.5 mole (76 parts) of a 50% aqueous solution of glycolic acid and 0.5 mole (185 parts) of amine mixture "A" was stirred for 8 hours in an xylene solution. The reaction mixture was then heated to 200° C. during a period of 9 hours. A total of 55 parts (3.5 moles) of water was collected. The final product, containing 7.0 percent of nitrogen, was a mixture of 2-hydroxy methyl, 3-alkyl substituted tetrahydropyrimidines corresponding to the formula:



where R'=10% hexadecyl, 10% octadecyl, 35% octadecenyl and 45% octadecadienyl.

Example 6

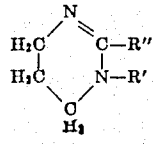
A mixture of 1.06 moles (380 parts) of naphthenic acid (acid number, 198) having an average molecular weight of about 280, and 1.06 moles (423 parts) of amine mixture "A" was refluxed in xylene solution for 4 hours. The reaction mixture was then slowly heated to 245° C. and was held at this temperature until the evolution of water ceased. Two moles (36 parts) of water were collected. Xylene was also removed with the water. The final product, containing 4.5 percent of nitrogen, is a mixture of 2,3-disubstituted tetrahydropyrimidines which correspond to the formula:



where R''=naphthenyl and R'=10% octadecyl, 10% hexadecyl, 35% octadecenyl and 45% octadecadienyl.

Example 7

Amine mixture "C" was used in place of amine mixture "A," following the procedure of Example 6. The final product also contains about 4.5 percent nitrogen. The final product is a mixture of 2,3-disubstituted tetrahydropyrimidines which correspond to the formula:



where R''=naphthenyl and R'=30% hexadecyl, 25% octadecyl and 45% octadecenyl.

Example 8

A mixture of 0.72 mol (200 parts) of naphthenic acid (acid number, 203) having an average molecular weight of about 275, and 0.72 mol (288 parts) of amine mixture "C" was refluxed in xylene solution for 4 hours. The reaction mixture was then slowly heated to 275° C. and was held at this emperature until the evolution of water ceased. About 1.4 mols (25 parts) of water were collected. The final product contains about 4.5% nitrogen and has the same formula as shown for Example 7.

Example 9

A mixture of 0.43 mol (100 parts) of naphthenic acid (acid number, 240) having an average molecular weight of about 230, and 0.43 mol (171 parts) of amine mixture "A" was refluxed in xylene solution for 4 hours. The reaction mixture was then slowly heated to 275° C. and was held at this temperature until the evolution of water ceased. About 0.86 mol (16 parts) of water were collected. The final product contains about 5.2% nitrogen and has a formula similar to Example 6.

Example 10

A mixture of 0.65 mol (200 parts) of naphthenic acid (acid number, 178) having an average molecular weight of about 297, and 0.65 mol (255 parts) of amine mixture "C" was refluxed in xylene solution for 4 hours. The reaction mixture was then slowly heated to 275° C. and was held at this temperature until the evolution of water ceased. About 1.2 mols (22 parts) of water were collected. The final product contains about 4.0% nitrogen and has a formula similar to Example 7.

Example 11

A mixture of 0.57 mol (200 parts) of naphthenic acid (acid number, 159) having an average molecular weight of about 330, and 0.57 mol (228 parts) of amine mixture "C" was refluxed in xylene solution for 4 hours. The reaction mixture was then slowly heated to 275° C. and was held at this temperature until the evolution of water ceased. About 1.2 mols (22 parts) of water were collected. The final product contains about 3.6% nitrogen and has a formula similar to Example 7.

Example 12

A mixture of 0.51 mol (232 parts) of naphthenic acid (acid number 122) having an average molecular weight of about 415, and 0.51 mol (202 parts) of amine mixture "C" was refluxed in xylene solution for 4 hours. The reaction mixture was then slowly heated to 275° C. and was held at this temperature until the evolution of water ceased. About 0.9 mol (16 parts) of water were collected. The final product contains about 3.1% nitrogen and has a formula similar to Example 7.

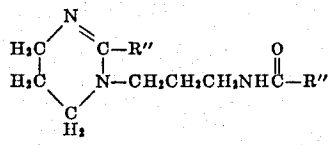
Example 13

A mixture of 0.6 mol (200 parts) of naphthenic acid (acid number, 159) having an average molecular weight of about 330, and 0.6 mol (182 parts) of amine mixture "B" were refluxed in xylene solution for 4 hours. The reaction mixture was then slowly heated to 275° C. and was held at this temperature until the evolution of water ceased. About 1.1 mols (20 parts) of water were collected. The final product contains about 3.6% nitrogen with a formula similar to Example 7.

Example 14

A mixture of 1.06 mols (300 parts) of naphthenic acid (acid number, 198) having an average molecular weight of about 280, and 0.53 mol (69.5 parts) of iminobispropylamine (dipropylene triamine), were refluxed in xylene solution for 4 hours. The reaction mix-

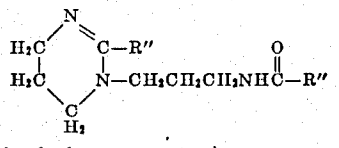
ture was then slowly heated to 275° C. and was held at this temperature until water was no longer evolved (2 hours). About 1.5 mols (27 parts) of water were collected. The reaction product is primarily comprised of 2-naphthenyl-2-naphthenamidopropyl tetrahydropyrimidines represented as:



wherein R'' is naphthenyl.

Example 15

A mixture of 1.0 mol (282 parts) of oleic acid and 0.5 mol (65.5 parts) of dipropylene triamine was refluxed in xylene solution for 4 hours. The reaction mixture was then slowly heated to 250° C. and was maintained at this temperature until the evolution of water ceased. About 1.5 mols (27 parts) of water were collected. The reaction product is predominantly comprised of a 2,3-disubstituted tetrahydropyrimidine represented as:

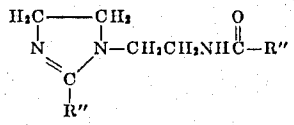


wherein R'' is oleyl.

IMIDAZOLINE-CONTAINING REACTION PRODUCTS

Example 16

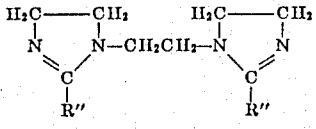
A mixture of 1.76 mols (500 parts) of naphthenic acid having an acid number of 198, and 0.88 mol (91 parts) of diethylene triamine were refluxed in xylene solution for 4 hours. The reaction mixture was then slowly heated to 275° C. and was held at this temperature until the evolution of water ceased (about 2 hours). Xylene was also removed along with the water. About 2.6 mols (47 parts) of water were collected. The reaction product is predominantly comprised of 1-naphthenamidoethyl - 2 - naphthenylimidazolines, corresponding to



wherein R'' is naphthenyl.

Example 17

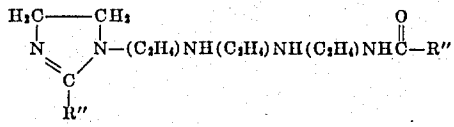
A mixture of 1.76 mols (500 parts) of naphthenic acid having an acid number of 198, and an average molecular weight of about 280, and 0.88 mol (129 parts) of triethylene tetramine were refluxed in xylene solution for 4 hours. The reaction mixture was then slowly heated to 300° C. and was held at this temperature until the evolution of water ceased (about 2 hours). Again, xylene was removed with the water. About 3.2 mols (57 parts) of water were collected. The reaction product is predominantly comprised of ethylene 1,1'-bis-2-naphthenylimidazolines represented as



wherein R'' is naphthenyl.

Example 18

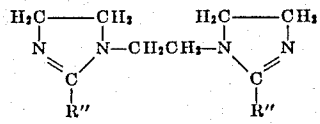
A mixture of 1.09 mols (300 parts) of naphthenic acid (acid number, 203) having an average molecular weight of about 275, and 0.545 mol (103 parts) of tetraethylene pentamine were refluxed in xylene solution for 4 hours. The reaction mixture was then slowly heated to 275° C. and was held at this temperature until water was no longer evolved (about 2 hours). About 1.7 mols (31 parts) of water were collected. The reaction product is primarily comprised of 1-naphthenamidotriethylenediimino-2-naphthenyl imidazolines represented as



wherein R'' is naphthenyl.

Example 19

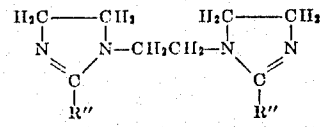
A mixture of 0.5 mol (142 parts) of stearic acid and 0.25 mol (36.5 parts) of triethylene tetramine were refluxed in xylene solution for 4 hours. The reaction mixture was then slowly heated to 275° C. and was held at this temperature until water was no longer evolved. About one mol (18 parts) of water was collected. The reaction product is predominantly comprised of ethylene 1,1'-bis-2-octadecyl imidazoline:



wherein R'' is octadecyl.

Example 20

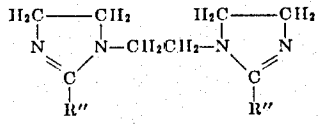
A mixture of one mol (282 parts) of oleic acid and 0.5 mol (73 parts) of triethylene tetramine were refluxed in xylene solution for 4 hours. The reaction mixture was then slowly heated to 275° C. and was held at this temperature until the evolution of water ceased. About 1.94 mols (35 parts) of water were collected. The reaction product is primarily ethylene, 1,1'-bis-2-octadecenyl imidazoline, represented as



wherein R'' is octadecenyl.

Example 21

A mixture of 0.5 mol (140 parts) of linoleic acid and 0.25 mol (36.5 parts) of triethylene tetramine were refluxed in xylene solution for 4 hours. The reaction mixture was then slowly heated to 275° C. and was held at this temperature until the evolution of water ceased. About one mol (18 parts) of water were collected. The reaction product is primarily ethylene 1,1'-bis-2-octadecadienyl imidazoline represented by

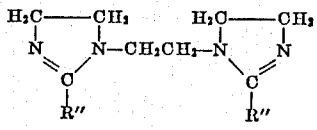


wherein R'' is octadecadienyl.

Example 22

A mixture of 0.5 mol (128 parts) of palmitic acid and 0.25 mol (36.5 parts) of triethylene tetramine were refluxed in xylene solution for 4 hours. The reaction mixture was then slowly heated to 275° C. and was held at this temperature until the evolution of water ceased. About one mol (18 parts) of water were collected. The

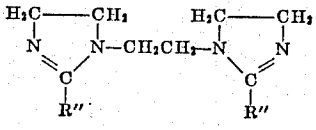
reaction product is primarily ethylene 1,1-'-bis-2-hexadecyl imidazoline represented by



wherein R'' is hexadecyl.

Example 23

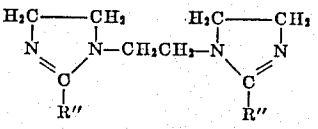
A mixture of 0.5 mol (114 parts) of myristic acid and 0.25 mol (36.5 parts) of triethylene tetramine were refluxed in xylene solution for 4 hours. The reaction mixture was then slowly heated to 275° C. and was held at this temperature until the evolution of water ceased. About one mol (18 parts) of water were collected. The reaction product is primarily ethylene 1,1'-bis-2-tetradecyl imidazoline represented as



wherein R'' is tetradecyl.

Example 24

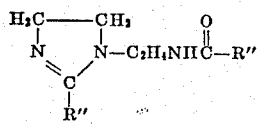
A mixture of 0.5 mol (100 parts) of lauric acid and 0.25 mol (36.5 parts) of triethylene tetramine were refluxed in xylene solution for 4 hours. The reaction mixture was then slowly heated to 275° C. and was held at this temperature until the evolution of water ceased. About one mol (18 parts) of water were collected. The reaction product is primarily ethylene 1,1'-bis-2-dodecyl imidazoline represented as



wherein R'' is lauryl, primarily dodecyl.

Example 25

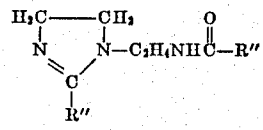
A mixture of 1.5 mol (25.8 parts) of normal capric acid and 0.75 mol (77.2 parts) of diethylene triamine were refluxed in xylene solution for 4 hours. The reaction mixture was then slowly heated to 275° C. and was held at this temperature until the evolution of water ceased. About 2.5 mols (45 parts) of water were collected. The reaction product is primarily 1-n-decylamidoethyl-2-n-decyl imidazoline represented as



wherein R'' is n-decyl.

Example 26

A mixture of 0.92 mol (300 parts) of a commercial abietic acid having an acid number of 170 and 0.46 mol (47 parts) of diethylene triamine, were refluxed in xylene solution for 4 hours. The reaction mixture was then slowly heated to 275° C. and was held at this temperature until the evolution of water ceased. About 1.5 mols (27 parts) of water were collected. The reaction product is predominantly comprised of a mixture of 1-abietyl amidoethyl-2-abietyl imidazolines represented as



wherein R'' is abietyl.

The effectiveness of the additives of this invention and of related products in stabilizing a typical fuel oil against sediment formation therein, is shown by screen-clogging test data. The amount of screen-clogging is determined with a Sundstrand V3 or S1 home fuel oil burner pump having a self-contained, 100-mesh Monel metal screen. About 0.05 percent, by weight, of a naturally-formed fuel oil sludge, composed of fuel oil, water, dirt, rust, and organic sediment, is added to ten liters of the fuel oil under test. This mixture is circulated by the pump through the screen for six hours. Then the sludge deposited on the screen is washed off with normal pentane, and filtered through a tared asbestos (Gooch crucible) filter. After it is dried, the material on the filter is washed with a 50–50 (volume acetone-methanol mixture. The total amount of organic sediment is determined by evaporating the n-pentane and the acetone-methanol filtrates, and weighing the residue. The weight of the material on the filter is the amount of inorganic sediment deposited. The sum of the weights of the organic and the inorganic deposits, in milligrams, gives the weight of sludge deposited, which weight is compared with the weight of sludge deposited from the uninhibited ("blank") fuel oil to determine the percent of screen-clogging. The uninhibited fuel oil, after six hours on test, effects 100 percent screen-clogging. Thus, the comparison percentagewise between the weight of sludge deposited by the uninhibited fuel oil and the inhibited fuel oil affords a measure of the percent of screen-clogging. The fuel oil used in the test is a blend comprising sixty percent (by weight) of catalytically cracked component and 40% of straight-run component, the blend having a boiling range from about 320° F. to about 640° F. The data obtained from said tests are provided in Table I.

TABLE I

Product of—Example, acid, amine	Conc., lbs./1,000 bbls.	Screen clogging, percent
(Uninhibited fuel oil blend)	0	100
(1) Oleic, "A"	50	12
(2) "D", "B"	25	1
(3) "E", "C"	25	4
(4) Glycine, "A"	25	2
(5) Glycolic, "A"	25	1
(6) Naphthenic, "A"	25	6
(7) Naphthenic, "C"	25	3
(14) Naphthenic, dipropylene triamine	10	15
(15) Oleic, dipropylene triamine	50	1
(15) Oleic, dipropylene triamine	25	3
(16) Naphthenic, diethylene triamine	50	12
(17) Naphthenic, triethylene tetramine	5	14
(18) Naphthenic, tetraethylene pentamine	10	2

As indicated above, the naphthenyl-substituted reaction products of this invention are also effective in inhibiting screen-clogging of hydrofined fuel oils. Tests corresponding to those described in connection with Table I were carried out with a hydrofined fuel oil having a boiling range from about 320° F. to about 640° F. Data obtained in such tests are shown in Table II.

TABLE II

Product of—Example, acid, amine	Conc., lbs./1,000 bbls.	Screen clogging, percent
(Uninhibited fuel oil)	0	100
(6) Naphthenic, "A"	10	10
(6) Naphthenic, "A"	25	5
(6) Naphthenic, "A"	50	10
(7) Naphthenic, "C"	25	10
(7) Naphthenic, "C"	50	4
(16) Naphthenic, diethylene triamine	25	5
(16) Naphthenic, diethylene triamine	50	9
(17) Naphthenic, triethylene triamine	10	20
(17) Naphthenic, triethylene triamine	25	8

A demonstration of the sediment inhibiting character of the additives contemplated herein and of related products is shown by results of 110° F. storage tests. In this test, a 500-milliliter sample of the fuel oil under test is placed in a convected oven maintained at 110° F. for a period of twelve weeks. Then, the sample is removed from the oven and is cooled. The cool sample is filtered through a tared asbestos filter (Gooch crucible) to remove the insoluble matter. The weight of such matter, in milligrams, is reported as the amount of sediment. In this test, a sample of the blank, uninhibited oil is run along with the fuel oil blend under test. The oil used is the same as that described above in connection with Table I. The effectiveness of a fuel oil composition containing an inhibitor is determined by comparing the test data therefor with the test data for the uninhibited, blank oil. Results of the storage tests are given in Table III.

Table III

Product of—Example, acid, amine	Conc., lbs./1,000 bbls.	Sediment, mg./liter
(Uninhibited fuel oil blend)	0	80
(1) Oleic, "A"	50	6
(Uninhibited fuel oil blend)	0	85
(2) "D", "B"	100	8
(Uninhibited fuel oil blend)	0	110
(3) "E", "C"	100	16
(Uninhibited fuel oil blend)	0	88
(4) Glycine, "A"	50	4
(Uninhibited fuel oil blend)	0	149
(5) Glycolic, "A"	100	10
(Uninhibited fuel oil blend)	0	68
(6) Naphthenic, "A"	50	6
(Uninhibited fuel oil blend)	0	65
(7) Naphthenic, "C"	100	7
(Uninhibited fuel oil blend)	0	24
(14) Naphthenic, dipropylene triamine	50	7
(Uninhibited fuel oil blend)	0	77
(15) Oleic, dipropylene triamine	50	14
(Uninhibited fuel oil blend)	0	68
(16) Napthhthenic, diethylene triamine	50	7
(Uninhibited fuel oil blend)	0	24
(17) Naphthenic, triethylene tetramine	50	6
(Uninhibited fuel oil blend)	0	120
(18) Naphthenic, tetraethylene pentamine	50	45

Sedimentation tests have also been carried out with an unstable, West Coast diesel fuel. This fuel had a 90 percent evaporation of 600° F. and an end point of 700° F. In the sedimentation test, described in connection with the data of Table III above, the uninhibited fuel formed 118 milligrams per liter. When a concentration of 100 pounds per M/bbls. of the product of Example 7 (naphthenic Acid-Mixture "C") was used in the fuel, the sediment value was only 20 milligrams.

Additional sedimentation tests of the same nature were made with the products of this invention, the base fuels being hydrofined fuel oils having boiling ranges from about 320° F. to about 640° F. Results of these tests are given in Table IV, following.

TABLE IV

Product of—Example, acid, amine	Conc., lbs./1,000 bbls.	Sediment, mgs./liter
(Uninhibited fuel oil)	0	13
(6) Naphthenic, "A"	10	9
(6) Naphthenic, "A"	25	7
(6) Naphthenic, "A"	50	7
(Uninhibited fuel oil)	0	10
(7) Naphthenic, "C"	10	3
(7) Naphthenic, "C"	25	4
(7) Naphthenic, "C"	50	3
(Uninhibited fuel oil)	0	10
(16) Naphthenic, diethylene triamine	25	4
(16) Naphthenic, diethylene triamine	50	3

As mentioned hereinabove, the additives of this invention are also excellent anti-rust agents. This is shown by results obtained by conducting A.S.T.M. Rust Test D-665 with the blank fuel oil blend and with the latter containing small amounts of typical additives of this invention and of related products. The fuel oil used is described above in connection with Table I. Results of such tests are set forth in Table V.

TABLE V

Product of—Example, acid, amine	Conc., lbs./1,000 bbls.	Rust test result
(Uninhibited fuel oil blend)	0	Fail.
(1) Oleic, "A"	50	Pass.
(3) "E", "C"	25	Do.
(5) Glycolic, "A"	10	Do.
(6) Naphthenic, "A"	50	Do.
(14) Naphthenic, dipropylene triamine	25	Do.
(16) Naphthenic, diethylene triamine	25	Do.
(17) Naphthenic, triethylene tetramine	25	Do.
(18) Naphthenic, tetraethylene pentamine	25	Do.

As indicated hereinabove, emulsion-forming tendencies of fuel oils containing certain additives militate against their use. While certain of the reaction products shown above, those not formed from naphthenic acids having molecular weights up to about 300 are effective sediment inhibitors and anti-screen-clogging agents, they do not inhibit emulsion formation. In fact, in some cases, the reaction products promote emulsion formation. In contrast, the related products prepared from naphthenic acids having molecular weights up to about 300 inhibit emulsification. This is demonstrated by the following test and test results.

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.

The fuel oil used in the emulsion tests is a blend comprising 80 percent of catalytically cracked component and

20 percent of straight run component, and having a boiling range (approximate) of 320–640° F. Results of the emulsion tests are shown in Tables VI and VII. In Table VI, distinction is drawn between products obtained from suitable naphthenic acids and acids of other types. In Table VII, distinction is drawn between naphthenic acids differing in molecular weight.

TABLE VI.—FUEL OIL EMULSION FORMATION TEST

Inhibitor, acid, amine	Conc., lbs./1,000 bbls.	Emulsion results
Uninhibited Fuel	0	Pass.
Ex. 6, Naphthenic, "A"	10	Do.
Do	25	Do.
Do	50	Do.
Ex. 7, Naphthenic, "C"	10	Do.
Do	25	Do.
Do	50	Do.
Ex. 14, naphthenic, dipropylene triamine	25	Do.
Ex. 15, oleic, dipropylene triamine	10	Fail.
Do	25	Do.
Do	50	Do.
Ex. 16, naphthenic, diethylene triamine	25	Pass.
Do	50	Do.
Do	100	Do.
Ex. 17, naphthenic, triethylene tetramine	25	Do.
Do	50	Do.
Ex. 18, naphthenic, tetraethylene pentamine	25	Do.
Ex. 19, stearic, triethylene tetramine	25	Fail.
Ex. 20, oleic, triethylene tetramine	25	Do.
Ex. 21, linoleic, triethylene tetramine	25	Do.
Ex. 22, palmitic, triethylene tetramine	25	Do.
Ex. 23, myristic, triethylene tetramine	25	Do.
Ex. 24, lauric, triethylene tetramine	25	Do.
Ex. 25, capric, diethylene triamine	25	Do.
Ex. 26, abietic, diethylene triamine	25	Do.

TABLE VII.—FUEL OIL EMULSION TEST

Inhibitor	Avg. mol. weight of naphthenic acid	Amine	Conc., lbs./1,000 bbls.	Emulsion results
Uninhibited fuel			0	Pass.
Example 6	280	"A"	10	Do.
Do	280	"A"	25	Do.
Do	280	"A"	50	Do.
Example 7	280	"C"	10	Do.
Do	280	"C"	25	Do.
Do	280	"C"	50	Do.
Example 8	275	"C"	25	Do.
Do	275	"C"	50	Do.
Example 9	230	"A"	25	Do.
Do	230	"A"	50	Do.
Example 10	297	"C"	25	Do.
Do	297	"C"	50	Do.
Example 11	330	"C"	25	Fail.
Do	330	"C"	50	Do.
Example 12	415	"C"	25	Do.
Do	415	"C"	50	Do.
Example 13	330	"B"	25	Do.
Do	330	"B"	50	Do.

From inspection of the data provided in Table VI, it is seen that only the products formed from naphthenic acids pass this emulsification test and that all other closely-related products fail in this test. Thus, the latter products are not attractive commercially for use in fuel oils, despite their behavior as anti-screen-clogging agents and sediment inhibitors. For example, Example 15 (oleic acid-dipropylene triamine) failed immediately in this test, emulsion being formed as soon as the fuel containing the product came in contact with water. Corresponding failures occurred with the fuels containing the products of Examples 19 through 25, inclusive.

In Table VII, it is shown that reaction products, formed from naphthenic acids having molecular weights ranging from about 230 to about 297 are satisfactory; whereas, those formed from similar acids having molecular weights from about 330 to about 415 are unsatisfactory.

In Table VII, it is shown that reaction products, formed from naphthenic acids having molecular weights ranging from about 230 to about 297 are satisfactory; whereas, those formed from similar acids having molecular weights from about 330 to about 415 are unsatisfactory.

Additional emulsification tests were carried out with a hydrofined fuel oil. The only difference between these tests and those carried out in regard to Table VI, was the substitution of a hydrofined fuel oil for the regular fuel oil. The hydrofined fuel oil had a range of approximately 320–640° F. Results of such tests are shown in Table VIII.

TABLE VIII.—FUEL OIL EMULSION FORMATION TEST

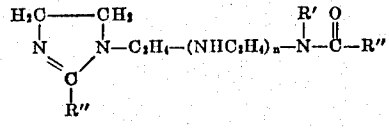
Inhibitor	Acid	Amine	Conc., lbs./1,000 bbls.	Emulsion results
Uninhibited fuel.			0	Pass.
Example 6	Naphthenic.	"A"	10	Do.
Do	do	"A"	25	Do.
Do	do	"A"	50	Do.
Example 7	do	"C"	10	Do.
Do	do	"C"	25	Do.
Do	do	"C"	50	Do.
Example 16	do	Diethylene triamine.	25	Do.
Do	do	do	50	Do.
Do	do	do	100	Do.
Example 17	do	Triethylene tetramine.	25	Do.
Do	do	do	50	Do.

Although the present invention has been described in conjunction 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. Such variations and modifications are considered to be within the scope and purview of the appended claims.

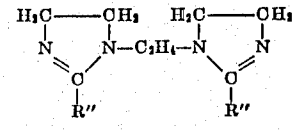
I claim:

1. A distillate fuel oil containing a small amount, sufficient to inhibit emulsification of the fuel oil with water, of a fuel-oil-soluble compound selected from the group represented by the general formulae:

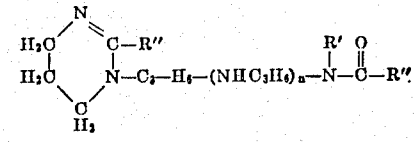
(I)



(II)

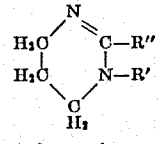


(III)



and

(IV)



wherein R' is selected from the group consisting of hydrogen and an aliphatic group having up to 18 carbon atoms and up to two double bonds, R'' is an unsubstituted naphthenyl group having a molecular weight up to about 300, and *n* is selected from zero and a small whole number.

2. A distillate fuel oil as defined by claim 1, wherein the naphthenic acid has a molecular weight from about 275 to about 300.

3. A distillate fuel oil as defined by claim 1, wherein the distillate fuel oil is a domestic heating fuel oil.

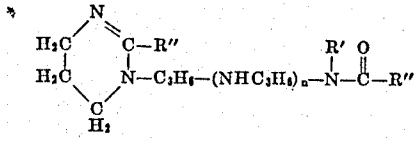
4. A distillate fuel oil as defined by claim 1, wherein the distillate fuel oil is a diesel fuel oil.

5. A distillate fuel oil as defined by claim 1, wherein the distillate fuel oil is a jet fuel.

6. A distillate fuel oil as defined by claim 1, wherein the distillate fuel oil is a hydrofined fuel oil.

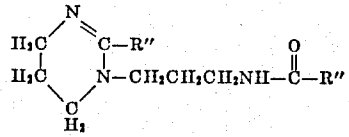
7. A distillate fuel oil as defined by claim 1, wherein the distillate fuel oil is a diesel fuel oil and the compound is present in an amount between about 0.005 percent and about 0.05 percent by weight.

8. A distillate fuel oil containing a small amount, sufficient to inhibit emulsification of the fuel oil with water, of a fuel-oil soluble compound represented by:



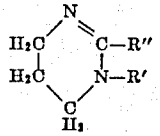
wherein R' is selected from the group consisting of hydrogen and an aliphatic group having up to 18 carbon atoms and up to two double bonds, R'' is an unsubstituted naphthenyl group having a molecular weight up to about 300, and *n* is selected from zero and a small whole number.

9. A distillate fuel oil containing a small amount, sufficient to inhibit emulsification of the fuel oil with water, of a fuel-oil-soluble compound represented by the formula



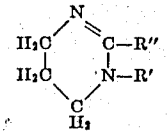
wherein R'' is an unsubstituted naphthenyl group having a molecular weight up to about 300.

10. A distillate fuel oil containing a small amount, sufficient to inhibit emulsification of the fuel oil with water, of a fuel-oil-soluble compound represented by the general formula



wherein R' is selected from the group consisting of hydrogen and an aliphatic group having up to 18 carbon atoms and up to two double bonds, and R'' is an unsubstituted naphthenyl group having a molecular weight up to about 300.

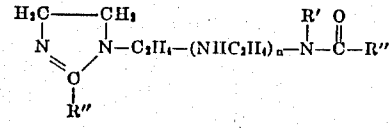
11. A distillate fuel oil containing a small amount, sufficient to inhibit emulsification of the fuel oil with water, of a fuel-oil-soluble compound represented by the formula



wherein R' is a mixture of aliphatic groups of which about 30 percent are hexadecyl, about 25 percent are octadecyl and about 45 percent are octadecenyl, and R'' is an unsubstituted naphthenyl group having a molecular weight up to about 300.

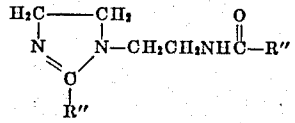
12. A distillate fuel oil containing a small amount, sufficient to inhibit emulsification of the fuel oil with water,

of a fuel-oil-soluble compound represented by the general formula



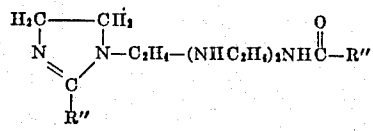
wherein R' is selected from the group consisting of hydrogen and an aliphatic group having up to 18 carbon atoms and up to two double bonds, R'' is an unsubstituted naphthenyl group having a molecular weight up to about 300, and *n* is selected from zero and a small whole number.

13. A distillate fuel oil containing a small amount, sufficient to inhibit emulsification of the fuel oil with water, of a fuel-oil-soluble compound represented by the formula



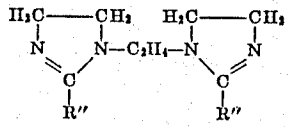
wherein R'' is an unsubstituted naphthenyl group having a molecular weight up to about 300.

14. A distillate fuel oil containing a small amount, sufficient to inhibit emulsification of the fuel oil with water, of a fuel-oil-soluble compound represented by the formula



wherein R'' is an unsubstituted naphthenyl group having a molecular weight up to about 300.

15. A distillate fuel oil containing a small amount, sufficient to inhibit emulsification of the fuel oil with water, of a fuel-oil-soluble compound represented by the formula



wherein R'' is an unsubstituted naphthenyl group having a molecular weight up to about 300.

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