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2,945,749

STABILIZED FUEL OIL CONTAINING TERTIARY ALKYL PRIMARY AMINES

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This invention relates to improved fuel oil compositions. More particularly, it is concerned with the provision of fuel oils which have been stabilized against the formation of color and sediment therein during storage.

Fuel oils in general are contemplated by the invention. The fuel oils with which this invention is especially concerned are hydrocarbon fractions having an initial boiling point of at least about 100° F. and an end point not higher than about 750° F., and boiling substantially continuously throughout their distillation range. Such fuel oils are generally known as distillate fuel oils. It will 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 (including hydrocracked) 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.

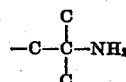
Especially contemplated herein are Nos. 1, 2 and 3 fuel oils used in domestic heating and as diesel fuel oils, particularly those made up chiefly or entirely of cracked distillate stocks. The domestic heating oils generally conform to the specifications set forth in A.S.T.M. Specifications D396-48T. Specifications for diesel fuels are defined in A.S.T.M. Specifications D975-48T. Also contemplated herein are fuels for jet combustion engines. Typical jet fuels are defined in Military Specification MIL-F-5624B.

As is well known, fuel oils have a tendency to deteriorate in storage and form colored bodies and sludge therein. 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 further 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

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the deterioration of the fuel oil during such storage would be a highly desirable and important contribution to the art. It is the principal object of the present invention to provide such a means. Other and further objects will be apparent from the following description of the invention.

In accordance with the present invention, it has now been found that oil deterioration in storage, with attendant formation of color and sludge in the oil, can be successfully inhibited by the addition to the oil of a small amount of a tertiary alkyl, primary, monoamine having from about 4 to 24 carbon atoms and in which the primary nitrogen atom is directly attached to a tertiary carbon atom. These amines all contain the terminal unit



Specific tertiary alkyl primary monoamines contemplated by the invention are, for example: tertiary butyl primary amine, tertiary octyl primary amine, tertiary decyl primary amine, tertiary dodecyl primary amine, tertiary tetradecyl primary amine, tertiary hexadecyl primary amine, tertiary octadecyl primary amine, tertiary eicosyl primary amine, tertiary docosyl primary amine and tertiary tetracosyl primary amine.

Mixtures of tertiary alkyl primary amines having from about 4 to about 24 carbon atoms are also highly suitable for use in the invention. A typical mixture of amines, for example is one comprised of tertiary alkyl primary amines of from about 12 to 15 carbon atoms, said mixture averaging about 12 carbon atoms per amine molecule. This mixture, designated hereinafter as "mixture A," contains, by weight, about 85% of tertiary dodecyl amine, about 10% of tertiary pentadecyl amine and relatively small amounts, i.e., less than about 5% of amines having less than 12 or more than 15 carbon atoms.

Another mixture of tertiary alkyl primary amines which is highly suitable for use in the invention is composed of tertiary alkyl primary amines of from about 18 to 24 carbon atoms and averaging about 20 carbon atoms per molecule. This mixture, designated hereinafter as "mixture B," contains the C₁₈-C₂₄ tertiary alkyl primary amines in about the following proportions:

	Percent
45 Tertiary octadecyl amine.....	40
Tertiary eicosyl amine.....	30
Tertiary docosyl amine.....	15
Tertiary tetracosyl amine.....	10
50 Other amines and non-amine.....	5

Amine mixtures, such as "mixture A" and "mixture B," as well as other suitable mixtures of tertiary alkyl primary amines of 4 to 24 carbon atoms, can be prepared by methods within the knowledge of those skilled in the art. For example, such mixtures may be prepared from polypropylene or polybutylene fractions or mixtures thereof. Thus, a selected polymer fraction composed of mixed polyolefins within a desired molecular weight range can be converted to the corresponding tertiary alkyl primary amines as follows: The selected polyolefin fraction is first hydrated by means of sulfuric acid and water to convert it to the corresponding alcohols. The alcohol mixture is then converted to alkyl chlorides by reaction with dry hydrogen chloride. Finally, the alkyl chloride mixture is condensed under pressure with ammonia to produce the tertiary alkyl primary amine mixture. Specific methods of preparing the tertiary alkyl primary amines are disclosed in the Journal of Organic Chemistry, vol. 20 (1955), page 295 et seq.

It is recognized that normal alkyl primary amines having the same number of carbon atoms as the tertiary alkyl primary amines contemplated herein have been

proposed heretofore for use in distillate fuel oils. This use, however, was for the purpose of imparting anti-screen clogging properties to the fuel oil. It will be appreciated that the problem of preventing screen clogging by such 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 which impart anti-clogging properties to fuel oil are able to inhibit 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. The mechanism by which the clogging is prevented involves the adsorption of the anti-clogging agent 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. On the other hand, additives which prevent the formation of sludge in the oil due to oxidative deterioration of the oil in storage, as above described, act by inhibiting the initial oxidation and the subsequent reactions which produce such sludge.

It is seen then that the prevention of screen-clogging by an oil and the prevention of sludge formation in an oil due to oil degradation depend on entirely distinct mechanisms. The ability of an additive to prevent screen-clogging will, therefore, in no way be indicative of its ability to prevent the formation of sludge sediment. As previously pointed out, the prevention of color and sludge formation in an oil, due to the oxidative deterioration of the oil, is of prime importance since it affects the quality of the fuel. As will be shown hereinafter, the tertiary alkyl primary amines of the present invention have outstanding ability over other aliphatic amines shown in the prior art with respect to the prevention of oil degradation and attendant sludge and color formation.

The outstanding effectiveness of the tertiary alkyl primary amines for the purpose of this invention is illustrated in the following examples and tests. These examples include fuel oil blends of representative tertiary alkyl primary amines and also for comparison purposes blends of representative normal alkyl and cyclic alkyl primary amines. All these blends were subjected to storage tests in order to determine the effectiveness of the various additives in inhibiting color and sediment formation in the oil. Two base fuel oils, A and B, were used in the blends prepared and tested. Both of these base oils were comprised of about 85% distillate stock derived from continuous catalytic cracking and about 15% of air-caustic sweetened straight-run distillate stock and had boiling ranges of from about 300° F. to about 640° F. Oil B, however, as will be seen from the data presented in Table I, was much more stable sediment-wise than oil A. This difference is due to the fact that the crude oil

charged to the cracking process in the manufacture of oil B contained a less amount of unstable components, phenols, thiophenols, pyrroles, etc., than the crude oil stock used to make oil A.

EXAMPLE 1

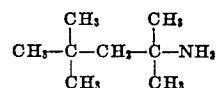
Normal heptyl amine was blended into the base fuel oil at a concentration of 10 pounds per 1000 barrels of the oil.

EXAMPLE 2

Normal octyl amine was blended into the base fuel oil at a concentration of 10 pounds per 1000 barrels of the oil.

EXAMPLE 3

Tertiary octyl primary amine having the formula



was blended into the base fuel oil at a concentration of 10 pounds per 1000 barrels of the oil.

EXAMPLE 4

Normal dodecyl amine was blended into the base fuel oil at a concentration of 10 pounds per 1000 barrels of the oil.

EXAMPLE 5

The tertiary alkyl primary amine "mixture A" (described hereinabove) was blended into the base fuel oil at concentrations of 10, 25, 50 and 100 pounds per 1000 barrels of oil.

EXAMPLE 6

Normal octadecyl amine was blended into the base fuel oil at a concentration of 10 pounds per 1000 barrels of the oil.

EXAMPLE 7

A mixture of normal primary aliphatic amines containing, by weight, about 30% n-hexadecyl amine, about 25% n-octadecyl amine and about 45% n-octadecenyl amine was blended with the base fuel oil at a concentration of about 10 pounds per 1000 barrels of the oil. This mixture is designated hereinafter as "mixture C."

EXAMPLE 8

The tertiary alkyl primary amine "mixture B" (described hereinabove) was blended with the base fuel oil at a concentration of 10 pounds per 1000 barrels of the oil.

EXAMPLE 9

A primary amine made from a modified rosln acid and composed essentially of abietyl amine was blended into the base fuel oil at a concentration of 10 pounds per 1000 barrels of the oil. This mixture is designated as "amine D."

EXAMPLE 10

Normal butyl amine was blended into the base fuel oil at a concentration of 25 pounds per 1000 barrels of the oil.

EXAMPLE 11

Tertiary butyl primary amine was blended into the base fuel oil at a concentration of 25 pounds per 1000 barrels of the oil.

Storage tests

The test used was the 110° F. storage test, which determines the characteristics of a fuel oil with respect to color and sediment formation in storage. 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 six 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 the in-

soluble 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 the fuel oil blend under test. The effectiveness of a fuel oil containing an inhibitor is determined by comparing the weight of the sediment formed in the inhibited oil with that formed in the uninhibited oil. The amount of color formed in the oil is measured in terms of the percentage of light transmitted by the oil after it is subjected to the storage test. The determination of light transmission involves the photoelectric measurement by means of a Lumetron colorimeter. The results of the various tests are shown in Table I.

It will be seen from the data in Table I that the tertiary alkyl primary amine additives substantially completely inhibit the tendency of the fuel oil to form sludge sediment during storage and at the same time improve the color characteristics of the oil. On the other hand, the straight-chained and cycloaliphatic amines, not only show no substantial inhibiting effect with respect to formation of sludge sediment, but they actually show an adverse effect in several instances. They also show an adverse effect on color formation, except in one instance where a very slight improvement was obtained.

It is evident from the data in Table I that the effectiveness of the tertiary alkyl primary amine of from 4 to 24 carbon atoms derives from the tertiary alkyl structure thereof, and, therefore, that any of the tertiary alkyl amines within the said carbon atom range will be effective for the purposes of the invention. Thus, tertiary butyl and tertiary octyl primary amines are highly effective, whereas the normal butyl and normal octyl amines are substantially ineffective. Also, several mixtures of amines within the prescribed carbon atom range are shown to be effective. On the other hand, single straight-chained amines and mixtures of such amines of comparable carbon atom range to the tertiary alkyl amines are ineffective.

TABLE I

Example Number	Amine Added	Number of Carbon Atoms	Concentration, Lbs./1,000 Bbls.	110° F. Storage Test (6 Weeks)	
				Sediment, Mg./Liter	Transmission
1	None (Base Fuel A)			49	57.6
2	n-Heptyl amine	7	10	55	28.2
3	n-Octyl amine	8	10	30.3	40.0
4	t-Octyl amine	8	10	7.0	68.1
5	n-Dodecyl amine	12	10	47.0	53.0
	t-Amine "Mixture A"	12-15 (Ave. 12)	10	2.0	83.1
	do	do	25	1.0	71.3
	do	do	50	1.0	72.8
	do	do	100	1.0	68.3
6	n-Octadecyl Amine	18	10	50.2	31.0
7	n-Amine "Mixture C"	18-18	10	51.0	61.8
8	t-Amine "Mixture B"	18-24 (Ave. 20)	10	4.0	82.4
9	Cyclo "Amine D"	19	10	48.0	59.4
10	None (Base Fuel B)			18.2	59.6
	n-Butyl amine	4	25	18.3	59.6
11	t-Butyl amine	4	25	7.6	69.6

The amount of tertiary alkyl primary amine additive used in the fuel oil can vary from about 2.5 to about 2500 pounds per 1000 barrels of the oil (i.e., about 0.001% to about 1.0%) depending upon the particular oil to be stabilized and the conditions of storage. Thus, the stability of a fuel oil, as indicated hereinbefore, depends largely upon the nature of the crude oil from which it is made and, therefore, some fuel oils will require more additive to stabilize them than others. Again caustic-treated oils, for example, will require less additive than untreated oils of similar character. As a general rule, however, the use of from about 10 to about 100 pounds of additive per 1000 barrels of oil (i.e., about 0.004 to about 0.04%) provides excellent results.

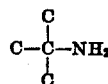
If desired, the fuel oil may also contain other additives designed to impart other improved characteristics to the oil. Thus, for example, foam inhibitors, anti-rust agents, burning and ignition quality improvers, etc., may be used in the oil.

Although the invention has been described and illustrated herein by means of specific examples, it is not intended that the scope thereof be limited in any respect thereby, but only as indicated by the following claims.

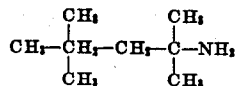
This application is a continuation-in-part of copending application, Serial No. 299,249, filed July 16, 1952, now abandoned.

What is claimed is:

1. A distillate fuel oil, containing a minor amount, sufficient to increase the color stability thereof and inhibit the formation of sediment therein during storage, of a tertiary alkyl primary monoamine containing from 4 to about 24 carbon atoms and characterized by the structural unit

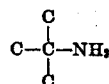


2. A distillate fuel oil, containing a minor amount, sufficient to increase the color stability thereof and inhibit the formation of sediment therein during storage, of the compound

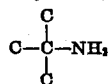


3. A distillate fuel oil, containing a minor amount, sufficient to increase the color stability thereof and inhibit the formation of sediment therein during storage, of an

alkyl primary monoamine containing 12 carbon atoms and characterized by the structural unit

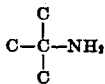


4. A distillate fuel oil, containing a minor amount, sufficient to increase the color stability thereof and inhibit the formation of sediment therein during storage, of an alkyl primary monoamine containing 18 carbon atoms and characterized by the structural unit



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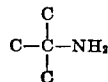
5. A distillate fuel oil, containing a minor amount, sufficient to increase the color stability thereof and inhibit the formation of sediment therein during storage, of a mixture of tertiary alkyl primary amines having from about 12 to about 15 carbon atoms and averaging about 12 carbon atoms per molecule, said amines being characterized by the structural unit



6. A distillate fuel oil, containing a minor amount, sufficient to increase the color stability thereof and inhibit the formation of sediment therein during storage, of a mixture of tertiary alkyl primary amines having from about 18 to about 24 carbon atoms and averaging about

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20 carbon atoms per molecule, said amines being characterized by the structural unit



7. A fuel oil subject to color degradation and oxidative deterioration containing, as a stabilizing agent, 0.001% to 1.0% of a tertiary alkyl primary monoamine in which the amino group is attached directly to a tertiary carbon atom.

References Cited in the file of this patent

UNITED STATES PATENTS

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2,684,292	Caron et al.	July 20, 1954
2,758,086	Stuart et al.	Aug. 7, 1956