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3,014,793

DISTILLATE FUEL OIL COMPOSITIONS

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This invention pertains to the stabilizing of petroleum oils against the formation and precipitation of sediment in storage. The invention relates to petroleum fuel oils and particularly to fuel oils known in the petroleum industry as gas oils, which are petroleum distillates intermediate in volatility between kerosene and lubricating oil and which are used as fuel in domestic heating furnaces and in diesel engines. These fuel oils are apt to form sediment in storage when they contain gas oils produced by cracking petroleum and particularly when they contain at least ten percent by volume of such gas oils of cracking origin. In accordance with the present invention the tendency for these fuel oils to form sediment is inhibited by incorporating in them small amounts of a tertiary alkyl primary amine wherein the alkyl radical is a hydrocarbon group containing at most 30 carbon atoms, at least eight carbon atoms and preferably 12 to 16 carbon atoms, of which at least one is tertiary and wherein the primary amino radical is attached to a tertiary carbon atom of said alkyl radical, a tertiary carbon atom being one that has three of its four valences fulfilled by chemical bonds with three other carbon atoms. The present invention is further concerned with fuel oil compositions containing said primary amines and also small amounts of surface-active compounds such as oil-soluble phosphates, alkyl phenol sulfides, sulfonates, naphthenates, amino-phosphatides, and phospho-sulfurized petroleum hydrocarbons. It relates to fuel oil compositions (1) that are stabilized against sediment formation, (2) that are stabilized against color degradation, and (3) that inhibit the corrosion of ferrous metals. Many of these fuel oil compositions are also characterized by the fact that they form little or no ash upon combustion.

Petroleum distillate fractions of the class of gas oil find wide use as fuel oils in the burner systems employed in domestic and industrial heating systems and as diesel fuels. It is common practice to incorporate cracked hydrocarbon stocks in these fuels, a fact which has given rise to a sediment formation problem. It has been found that the use of 10% by volume or more of cracked stocks in these hydrocarbon fuels causes the formation of sludge or sediment during the time the fuel is in storage, and this sediment then later causes plugging or fouling of the filters, lines and nozzles in the burner systems in which they are employed. It has further been found that the formation of sediment is often accelerated by the presence of copper, a metal that is used extensively in many fuel oil systems.

Several other problems have also been encountered with distillate fuels. These problems include the corrosion of ferrous metals such as carbon steel, cast iron, etc., with which the fuels come in contact. The degree of corrosion is particularly noticeable when the metals are contacted by the fuels in the presence of water or an atmosphere containing water vapor. Further, some materials that have been added to these fuels to stabilize them against sediment formation have given rise to emulsion problems, occasioned when fuels containing these additives are contacted and agitated with water. It has been found that certain additives under these conditions cause the water and oil to form emulsions that are extremely stable and difficult to resolve. Finally, it is desirable to have these fuel oils be stable against any color degradation.

Accordingly, it is a primary object of the present invention to improve the stability of petroleum fuel oils against the formation of sediment, when these fuels contain 10%

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or more by volume of cracked stocks. The particular oils embraced by the present invention include the fuel oils falling within A.S.T.M. specification, D-396-48T, for fuel oils (grades 1 and 2). Also useful in accordance with the present invention are diesel fuel oils No. 1-D, No. 2-D, and No. 4-D of A.S.T.M. specification D-975-51T.

Additional objects of the present invention include improving the color stability and the anti-corrosion characteristics of these oils, and also minimizing or completely eliminating the formation of ash from the improving additives when the improved fuels are burned.

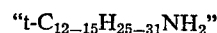
In accordance with the present invention, fuel oils are stabilized against sediment formation by the addition of from about 0.001 to 1.0 wt. percent of a primary amine in which the carbon atom attached to the amino group is a tertiary carbon atom.

Tertiary alkyl primary amines suitable for use in accordance with the present invention can be prepared from tertiary olefins, for example polymers of propylene or isobutene and from copolymers of propylene and isobutene, as well as from copolymers of isobutene and butenes or pentenes.

Such polymers and copolymers are well known synthetic olefins in the petroleum industry. For instance, propylene polymers ranging in molecular size from the dimer of six carbon atoms to the tetramer of twelve carbon atoms are made, in mixtures of suitable volatility for use in motor gasoline, by polymerizing propylene in the presence of catalysts which are made by impregnating silica gel suitably with phosphoric acid. Also, in the manufacture of iso-octane for use in aviation gasoline, isobutene has been converted to diisobutene by polymerization with sulfuric acid as catalyst and then to iso-octane by hydrogenation. Of course, the manner of preparation of the polymers or olefins is not at the point of novelty of the present invention, nor is the manner of preparation of primary amines from olefins, which as is well known, can be aminated with ammonia. Suffice it to say that an olefin like the dimer of isobutene can be converted, for example, to 2-amino-2,4,4-trimethyl-pentane and 2-amino-2,3,4-trimethyl-pentane, each of which is a primary amine having an amino radical attached to a tertiary carbon atom in an alkyl group of eight carbon atoms arranged in a branched chain.

In both of the examples above, the amino radical is attached to a tertiary carbon atom which is actually the second carbon atom in the longest chain of the alkyl group. That is a normal attachment when the alkyl group is derived from a polymeric olefin which naturally tends to end with a double bond; but even though that structure naturally predominates there occur various isomerizations and migrations through which other structures result and produce double bonds elsewhere than at the end of the longest chain. In a polymerization not only structural variations but also irregularities of molecular weights occur; and at any given set of conditions of reaction the final equilibrium produces a mixture of olefins.

Consequently, the tertiary alkyl primary amines, suitable for use in accordance with the present invention, when they are made from tri-isobutene, which is a polymer of isobutene having tertiary carbon atoms in a molecule containing 12 carbon atoms, may contain some tertiary alkyl amines of 13, 14 and/or 15 carbon atoms as well as the predominant one of 12 carbon atoms. Such a mixture is conveniently designated as



a tertiary alkyl primary amine having predominantly 12 carbon atoms per molecule and having minor proportions of homologous molecules with 13, 14 and/or 15 carbon atoms. Similarly, when making a suitable tertiary alkyl primary amine of 18 carbon atoms from hexa-propylene,

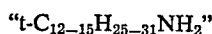
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a polymer of propylene, one obtains a mixture conveniently designated as "t-C₁₈₋₂₄H₃₇₋₄₉NH₂," which in context is understood to be a tertiary alkyl primary amine having predominantly 18 carbon atoms per molecule and having minor proportions of homologous molecules with 19, 20, 21, 22, 23 and/or 24 carbon atoms.

Specific examples of tertiary alkyl primary amines suitable for use in accordance with the present invention are the following:

6-amino-2,2,4,4,6,8,8-heptamethyl-nonane
2-amino-2,3,4,6,6,8,8-heptamethyl-nonane
4-amino-2,3,4,6,6,8,8-heptamethyl-nonane
4-amino-2,4,6-trimethyl-nonane
3-amino-3,5,8-trimethyl-nonane
3-amino-3,4,6-trimethyl-nonane
3-amino-3,6-dimethyl-decane
3-amino-3,5-dimethyl-decane
4-amino-4-methyl-undecane
4-amino-2,4,6,8,10-pentamethyl-tridecane
3-amino-3,5,7,9,12-pentamethyl-tridecane
5-amino-5,13-dimethyl-hexadecane

Specially preferred for use in accordance with the present invention is the material designated as



which was made from tetrapropylene and which by actual analysis upon degradation to its constituent olefin by reaction with nitrous acid was shown to consist essentially of tertiary dodecyl primary amine. Particularly preferred concentrations of amines in a fuel are from 0.005 to 0.2 wt. percent and especially 0.005 to 0.02 wt. percent.

While the fuel oil compositions described above are particularly stabilized against sediment formation, the quality of the compositions can be further improved by the addition of certain surface-active compounds, particularly the oil-soluble phosphates, amino-phosphatides, and phospho-sulfurized petroleum hydrocarbons. All of these compounds have detergent properties, and some of them are also rust preventives.

Oil-soluble phosphates suitable for the purposes of the present invention include phosphoric acid esters of aliphatic alcohols having from 6 to 20 carbon atoms. Any such ester may be a single species or a mixture of mono- or di-esters of primary and secondary alcohols with various phosphoric acids. Especially attractive alcohols for preparing the phosphoric acid esters are the C₅-C₁₃ "Oxo-alcohols," which are conventionally prepared from C₄ to C₁₂ olefins by the well known Oxo process. In accordance with the Oxo process an olefin is reacted with carbon monoxide and hydrogen at 2000-4000 p.s.i.g., and 225°-400° F., in the presence of a cobalt-type catalyst to form an aldehyde with one or more carbon atom than is possessed by the initial olefin. The aldehyde is then hydrogenated to the corresponding aliphatic alcohol. It will be noted that the alcohols produced by this process are primary alcohols with relatively large proportions of branched chains.

In petroleum refineries the olefins employed in the Oxo process are conventionally formed by polymerizing and copolymerizing olefins such as ethylene, propylene and the various butylenes. A typical plant stream, for example, may contain 15-60 mol percent of propylene, 0.5-50 mol percent of n-butenes, 0.1-10 mol percent of i-butylene and trace amounts of other hydrocarbons. It will be appreciated that the product formed by polymerizing such a stream will consist of a large number of olefins having various molecular weights and structural configurations. The polymerization may be carried out at 300°-500° F., and 250-5000 p.s.i.g. in the presence of a phosphoric acid catalyst. Illustrative of the type of

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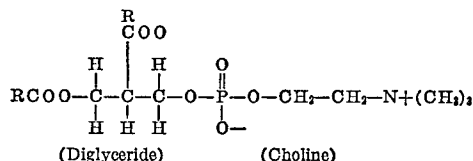
alcohols obtained by the oxonation of C₇ olefins (in turn obtained by the polymerization of a mixture of C₃ and C₄ olefins) is the following analysis of a "C₈ Oxo alcohol."

Constituent alcohol:	Percent
3,5-dimethyl hexanol -----	29
4,5-dimethyl hexanol -----	25
3,4-dimethyl hexanol -----	17
5-methyl heptanol -----	16
3-methyl heptanol -----	
4-ethyl hexanol -----	2.3
5,5-dimethyl hexanol -----	1.4
2-alkyl alkanols -----	4.3
Others -----	5.0

The C₆-C₂₀ aliphatic alcohols may be esterified with phosphoric acid in any conventional manner. The Oxo alcohol-phosphoric acid esters are preferred and especially the C₈ Oxo phosphoric acid esters. A particularly attractive alkyl phosphate is the di-alkyl C₈ Oxo ester of phosphoric acid hereinafter designated as Additive LR.

Especially effective sulfonates are the oil-soluble ammonium petroleum sulfonates and the oil-soluble alkyl benzene sulfonates with which the preferred amines can act synergistically for stabilizing the oils against sediment formation in the presence of metals. Preferred sulfonates are those derived from petroleum sulfonic acids having molecular weights of about 380 to 550.

Preferred surface-active agents for use with the primary amines described earlier are the oil-soluble phosphatides including the various lecithins which are the choline-phosphoric-acid mono-esters of the diglycerides of oleic, stearic or palmitic acid and which have the general structural formula:



in which the RCO groups are oleoyl, searoyl, palmitoyl, or other acyl radicals of fatty acids. Lecithin is readily available as such in a commercial grade that contains amounts of other phosphatides such as cephalin and lipositol. This commercial grade is very effective in the compositions of the present invention.

Phospho-sulfurized hydrocarbons that are employed in conjunction with the amines of the present invention may be prepared by treating hydrocarbons having a viscosity above about 50 S.S.U. @ 210° F. with from 5 to 25 wt. percent of a phosphorus sulfide at a temperature of 375° to 475° F. and preferably 400° to 430° F. It is preferred that from 10 to 20 wt. percent of the phosphorus sulfide be employed and that the time of treatment be from 1 to 20 hours. The reaction is preferably continued for several hours, for example, 10 hours or so, and until the hydrocarbon product has a phosphorus content of about 2% to 6% by weight and a sulfur content of about 5% to 12% by weight. The treatment should not be extended to the point where the product becomes insoluble in the fuel oil in which it is to be used.

Preferred hydrocarbons for phospho-sulfurization are lube oil base stocks and especially bright stocks having for example an S.S.U. viscosity at 210° F. in the range from about 150 to 250 seconds. They may be obtained, for example, by deasphalting, dewaxing, acid-treating, clay-treating, etc. of various petroleum residua. The higher molecular weight paraffins, aromatics, cyclic aliphatics, alkaryl compounds and the like may be used. Petrolatums, waxes, solvent extracts of petroleum fractions, etc. are also suitable.

The phospho-sulfurized hydrocarbons are preferably neutralized to reduce their titratable acidity and thereby

increase their stability. Their instability is evidenced by a high degree of corrosiveness toward copper and also by an objectionable odor.

The titratable acidity of the phospho-sulfurized hydrocarbons may be reduced by treatment with suitable basic reacting compounds such as the hydroxides, carbonates or oxides of alkali or alkaline earth metals, ammonia, alkyl or aryl substituted ammonia compounds such as amines or guanidine and derivatives thereof. Stability may also be improved by treatment with about 2 to 50 weight percent based on the total material of a suitably active olefinic hydrocarbon. By "suitably active" is meant that the olefinic material has the property of reacting with loosely bound sulfur in the phospho-sulfurized oil. Preferred olefins include the terpenes, terpineol, and the like and olefinic hydrocarbons such as isobutylene, diisobutylene, and the more reactive of the analogous aliphatic and cycloaliphatic materials. Such a process is described in U.S. Patent 2,640,053.

These ingredients may be mixed together at temperatures of 60° to 400° F. and from about 1 to 10 hours until the desired degree of stability is attained. The reaction time may be as much as 20 hours.

Again, the stability may be improved by treatment with about 0.1 to 5.0% and preferably 0.5 to 2.0 wt. percent of an unsaturated ester based on the phospho-sulfurized hydrocarbon. Preferred unsaturated esters are unsaturated alcohol esters of monocarboxylic acids, which may be prepared by conventional esterifying means. This is described in U.S. Patent 2,694,044.

Concentrations of 0.001 to 0.5 wt. percent of the various types of surface-active agents described above are suitable for use in conjunction with primary amines of the type defined by the present invention. Particularly preferred concentrations of such surface-active agents are from 0.001 to 0.05 wt. percent of a heating oil and especially 0.002 to 0.010 wt. percent.

The various additives mentioned above, both of the amine and surface-active types, may be added directly to a fuel oil as such or in the form of an oil-soluble concentrate. A suitable oil solvent for the preparation of a concentrate is preferably an oil of good quality, for example, a solvent-extracted paraffinic or Mid-Continent neutral oil falling within a viscosity range at 210° F. of 30 to 120 S.U.S. or a stable fuel oil of any of the grades hereinbefore designated.

Of the various amine additives described herein, the $t\text{-C}_{12-15}\text{H}_{25-31}\text{NH}_2$ additive is especially preferred. Of the various surface-active additives to be used in combination with the amine additives and especially the amine additive just named, the lecithin additive is particularly preferred.

The nature of this invention will be more fully understood from the following examples:

EXAMPLE I

A conventional heating oil was tested for stability against sediment formation as the oil was received and again after addition of various types of additives to the oil. The oil in this example and in all of the following examples was a blend consisting of about 30% by volume of catalytically cracked stock, about 50% by volume thermally cracked stock, and about 20% by volume of virgin stock. Typical inspections of this type of oil, for which the respective components may be varied from 10 to 50%, 10 to 50% and 5 to 80% in the order named above, are as follows:

Gravity, ° A.P.I. -----	32
Color, Robinson -----	13
Pensky-Martens flash, ° F. -----	150
Sulfur, wt. percent -----	0.8
Neutralization number -----	0.03
Aniline point, ° F. -----	137

A.S.T.M. distillation range:

I.B.P., ° F. -----	330
10% -----	420
50% -----	500
90% -----	585
Final boiling point, ° F. -----	645
Conradson carbon residue -----	Trace

Typically, these fuel oils boil between the limits of 300° F. and 700° F.

The stability characteristics of this heating oil by itself, and in combination with various amine additives, are indicated in the following table. In each instance the oil sample or blend was heated for a period of either 16 hours at 210° F. or for 14 days at 150° F., and the amounts of sediment formed during these heating periods were then isolated and measured.

Table I

HEATING OIL STABILITY TESTS—(SEDIMENT FORMATION)—EVALUATION OF INHIBITORS

No.	Blend Tested	Mg. sediment/600 g. oil	
		16 hrs. at 210° F.	14 days at 150° F.
1.....	Heating oil, uninhibited.....	32.8	26
2.....	+0.1% $t\text{-C}_{12-15}\text{H}_{25-31}\text{NH}_2^1$	1.2	1.5
3.....	+0.04% $t\text{-C}_{12-15}\text{H}_{25-31}\text{NH}_2^1$	1.1	1.6
4.....	+0.01% $t\text{-C}_{12-15}\text{H}_{25-31}\text{NH}_2^1$	0.9	1.6
5.....	+0.005% $t\text{-C}_{12-15}\text{H}_{25-31}\text{NH}_2^1$	2.4	2.4
6.....	+0.002% $t\text{-C}_{12-15}\text{H}_{25-31}\text{NH}_2^1$	10.4	6.6
7.....	+0.50% straight-chain aliphatic primary amine ²	59.4	78.1
8.....	+0.1% straight-chain aliphatic primary amine ²	25.9	39.6
9.....	+0.5% straight-chain aliphatic primary amine ³	74.3	116.2
10.....	+0.1% straight-chain aliphatic primary amine ³	55.7	42.7

¹ $t\text{-C}_{12-15}\text{H}_{25-31}\text{NH}_2$ hereinafter identified as Additive P.

² A mixture of straight chain primary amines having the following approximate composition:

	Percent
$\text{C}_{12}\text{H}_{25}\text{NH}_2$ -----	90
$\text{C}_{14}\text{H}_{29}\text{NH}_2$ -----	9
$\text{C}_{18}\text{H}_{35}\text{NH}_2$ -----	1

³ A mixture of straight chain primary amines having the following approximate composition:

	Percent
$\text{C}_{10}\text{H}_{21}\text{NH}_2$ -----	90
$\text{C}_{18}\text{H}_{37}\text{NH}_2$ -----	6
$\text{C}_{18}\text{H}_{35}\text{NH}_2$ -----	4

Referring to the above table, it will be noted that the addition of small amounts of a primary amine containing a tertiary carbon atom immediately adjacent the amino group to a heating oil markedly reduces the sediment forming tendencies of the heating oil. It will also be noted that the addition of straight-chain alkyl primary amines containing no such tertiary carbon atom to a heating oil does not improve the stability of the oil, but instead, actually renders it less stable. The latter type of amines have found wide application as wetting agents, rust preventives, and demulsifiers in various oil fractions; but it is apparent from Table I above, that these amines are far inferior to the amines disclosed in the present invention for stabilizing heating oils against sediment formation. It will also be noted that concentrations of the amines of the present invention in excess of 0.005 wt. percent are very effective in reducing the amount of sediment formed by a heating oil containing cracked stocks. When a concentration of the amine is at least 0.01%, the stabilizing influence is especially pronounced.

EXAMPLE II

A heating oil of the same type and source as that employed in Example I was blended with an amine of the type defined in the present invention along with small amounts of oil-soluble surface-active agents. The various blends were then subjected to a number of different tests to determine their color stability, sludging tendency, emulsion stability, and rust-preventive ability.

The color stability of the oil and of the various oil-

inhibitor blends was determined by heating an appropriate sample for a period of 16 hrs. at 210° F., in one test procedure, and for 14 days at 150° F. in a second test procedure. Following the heating period, each sample was filtered and the percentage of white light transmitted through the filtered oil was determined and compared with the amount of white light transmitted through the sample before heating.

The sediment forming tendencies of the samples were also ascertained by two procedures. A first procedure consisted of heating a sample for a period of 16 hrs. at 210° F., and then determining the weight of sediment formed during this period. According to a second test procedure a sample was heated for 14 days at 150° F. and the weight of sludge accumulating during this period then quantitatively determined.

The emulsion stability of the oil samples was determined by shaking each sample with 10% by volume of water for 60 seconds. The time necessary for an oil to regain clarity after this shaking step is a direct measure of the stability of the emulsion that the oil will form with water in actual processing and handling operations.

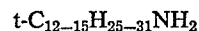
The rusting tendency of oil samples was determined by mixing each sample with 10% by volume of water; then shaking for 30 seconds; adding a polished mild steel (SAE #1020) test panel and shaking again for 30 seconds. The extent of rusting in both the water layer and the water-saturated oil layer was observed after room temperature aging of approximately one month.

The sediment and color stability tests were run both in the presence and absence of copper.

The effectiveness of the amines alone and in combination with oil-soluble surface-active agents is clearly indicated in the following table, where the results of the various tests described above are listed.

It will be noted that Additive P, which is in reality $t\text{-C}_{12-15}\text{H}_{25-31}\text{NH}_2$, is a particularly attractive amine to use as a fuel oil additive. It greatly reduces sediment formation in the absence of copper. It also markedly increases the color stability of fuel oil and decreases the stability of the emulsions that a fuel oil forms with water.

It will also be noted that small amounts of a tertiary alkyl primary amine in combination with a surface-active agent of the types described earlier herein greatly enhance the quality of a fuel oil. Not only is the sediment-forming tendency of the fuel oil reduced, but other properties of the oil are also improved. For example,



and lecithin, when jointly added to a fuel oil, decrease the fuel oil's sediment- and color-forming tendencies and also greatly improve its resistance toward rust and emulsion formation. In addition, this particular additive composition has a synergistic effect in reducing the sediment-forming tendency of a fuel in the presence of copper. It is also characterized by the fact that it is substantially non-ash-forming since it does not contain any metal constituents.

It is apparent from Table II that other tertiary alkyl primary amines such as $t\text{-C}_{13-24}\text{H}_{37-49}\text{NH}_2$ are effective in increasing the stability of petroleum fuel oils. It is also apparent that the effectiveness of these amines is increased by small amounts of surface-active agents such as the alkyl esters of phosphoric acid.

EXAMPLE III

Samples of a heating oil of the same type as that employed in Examples I and II, but having slightly different stability characteristics were blended with an amine of

Table II

	Conc. of Additive in Heating Oil, Wt. percent	Mg. insoluble sediment/600 g. Oil				Color Stability				Rusting Tendency		Emulsion Stability
		16 hrs. at 210° F.		14 days at 150° F.		16 hrs. at 210° F.		14 days at 150° F.		Water Phase	Oil Phase	
		No Cu	With Cu ¹	No Cu	With Cu	No Cu	With Cu	No Cu	With Cu			
1	No Additive	32.8	82.7	26	21.9	79	45	71	68	heavy	heavy	1 day.
2	0.005 Additive P	2.4		2.4		86		80		do	do	ca. 3 hrs.
3	0.01 Additive P	0.9	76.2	1.6	16.7	87	33	86	49	do	do	Do.
4	0.02 Additive P	0.8	{ 54.4	1.6	{	91	{ 33	84	{	v. heavy	do	
		1.4		1.5		85		79				
5	0.04 Additive P	1.1		1.6		91		90		heavy	trace	2 days.
6	0.10 Additive P	1.2		1.5		87		86		trace	none	1 day.
7	0.005 Additive J ²	3.1	65.0	3.8	21.0	72	23	73	56	heavy	heavy	
8	0.01 Additive J	1.5	91.0	1.0	25.2	81	20	77	46	do	do	
9	0.005 Lecithin	32.2	55.3	22.4	42.9	78	57	68	65	none	light	
10	0.01 Lecithin	20.1	46.2	10.4	53.6	74	61	62	62	do	none	
11	0.02 Lecithin	2.2	4.8	5.9	18.1	49	34	58	59	medium	light	
12	0.04 Lecithin	1.6	2.6			62		39		do	none	
13	0.01 Additive LR	48.6		56.7		61		52		none	do	<1 day.
14	0.005 Additive P	{ 2.1	{ 44.2	{ 2.7	{ 15.6	{ 86	{ 47	{ 83	{ 66	{ do	{ do	{ ca. 3 hrs.
15	0.005 Lecithin											
	0.01 Additive P	{ 0.7	{ 14.8	{ 0.6	{ 2.2	{ 85	{ 38	{ 80	{ 52	{ do	{ trace	{ Do.
16	0.01 Lecithin											
	0.02 Additive P	{ 0.9	{	{ 1.0	{	{ 86	{	{ 84	{	{ do	{ none	{ Do.
17	0.01 Lecithin											
	0.04 Additive P	{ 0.9	{	{ 1.0	{	{ 92	{	{ 85	{	{ do	{ do	{
18	0.01 Lecithin											
	0.02 Additive P	{ 1.3	{	{ 1.6	{	{ 93	{	{ 84	{	{ do	{ do	{ Do.
19	0.005 Additive LR											
	0.02 Additive P	{ 1.0	{	{ 1.4	{	{ 88	{	{ 81	{	{ do	{ do	{ Do.
20	0.01 Additive LR											
	0.01 Additive P	{ 3.1	{	{ 3.6	{	{ 77	{	{ 82	{	{ do	{ do	{ Do.
21	0.01 Additive LR											
	0.01 Additive J	{ 0.9	{ 9.3	{ 0.9	{ 1.5	{ 80	{ 26	{ 76	{ 62	{ heavy	{ medium	{
	0.01 Lecithin											

¹ 1/2" x 6" copper sheet immersed in oil during heating.

² Additive J: $t\text{-C}_{13-24}\text{H}_{37-49}\text{NH}_2$.

As may be seen in Table II, small concentrations of a tertiary alkyl primary amine are very effective in reducing the sediment forming tendency and increasing the color stability of a petroleum distillate fuel oil. Where the concentration of such an amine is about 0.1%, based on the fuel oil, this additive imparts some rust preventive properties to the oil.

the type defined in the present invention. Samples were also blended with small amounts of phospho-sulfurized hydrocarbons and with ammonium sulfonate in the presence and absence of the amine. The resulting blends and samples were then evaluated for their color- and sediment-forming tendencies. The results of the necessary tests are shown in Table III.

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Table III

	Blend, Wt. Percent Additive	Insoluble Sediment ¹		Color Stability ²	
		No Cu	With Cu ³	No Cu	With Cu
1----	100% Heating Oil.....	35.2	65.3	81	48
2----	0.02% Additive P.....	1.4	54.4	85	33
3----	0.02% Additive LB ⁴	27.8	69.6	35	43
4----	0.05% Additive LB.....	20.5	48.1	13	25
5----	0.01% LB.....	1.4	10.2	83	37
6----	0.01% Additive P.....	3.9	22.1	87	41
7----	0.01% Ammonium Sulfonate ⁵	7.4	19.6	84	57
8----	0.02% Ammonium Sulfonate ⁵	51.6	129.0	45	25
9----	0.02% Ammonium Sulfonate ⁶	73.1	74.0	37	37

¹ Mg. sediment per 600 g. oil after heating 16 hrs. at 210° F.

² Percent transmission of white light through filtrate after heating 16 hrs. at 210° F. relative to unheated oil as 100%.

³ 1 1/2" x 6" copper sheet immersed in oil during heating.

⁴ (170 SSU visc. at 210° F. bright stock+10% P₂S₅)+4% vinyl acetate.

⁵ Oil solution containing 33 1/3% ammonium petroleum sulfonate.

⁶ Oil solution containing 50% ammonium petroleum sulfonate.

The data in Table III again clearly indicate that an amine of the type defined in the present invention is very effective in stabilizing a fuel oil. The data also indicate that a fuel oil is stabilized even more effectively by the addition of small amounts of a phospho-sulfurized hydrocarbon or of ammonium sulfonate along with the amine. In fact, the amine co-acts synergistically with either of these two surface-active agents in stabilizing a fuel oil in the presence of copper.

EXAMPLE IV

A number of diesel fuel oils and a heavy catalytic cycle oil were subjected to the same sediment, color and rust tests as were employed in Examples I, II and III. Each oil was also blended with 0.014 wt. percent of an additive comprised of one part of t-C₁₂₋₁₅H₂₅₋₃₁NH₂ and one part of commercial lecithin by weight and again subjected to the same test procedures. The results of these tests are given in Table IV below. It will be noted that each of the diesel fuel oils contained cracked stocks and met with various accepted specifications for such fuels. In the table, each of the diesel fuels is identified by the particular set of specifications that it meets.

Table IV
DIESEL FUEL STABILIZATION

Fuel Sample	Fuel Type	Insoluble Sediment, mg./600 cc.		Color Stability		Rust Test	
		No Copper	With Copper	No Cu	With Cu	Water Phase	Oil Phase
A-----	ASTM 975-51T (2-D)-----	17.7	44.6	97	90	Heavy-----	Medium.
A+Additive ¹ -----	do-----	1.6	14.0	100+	86	None-----	None.
B-----	do-----	9.9	8.3	84	73	Trace-----	Do.
B+Additive-----	do-----	0.9	1.3	85	48	None-----	Do.
C-----	ASTM 975-51T (4-D)-----	10.4	32.0	81	67	Light-----	Light.
C+Additive-----	do-----	1.0	0.9	100+	100+	None-----	None.
D ² -----	MIL-F-896 (Class 1)-----	9.2	42.9	-----	-----	Medium-----	Medium.
D+Additive-----	do-----	1.6	9.4	-----	-----	None-----	None.
E ³ -----	-----	16.3	18.4	-----	-----	v. Heavy-----	v. Heavy.
E+Additive-----	-----	1.3	10.9	-----	-----	None-----	None.

¹ Additive in all cases is 1:1 t-C₁₂₋₁₅H₂₅₋₃₁NH₂ and lecithin (commercial grade).

² Fuel D corresponds to MIL-F-896 (Class 1) except that it contains 30% of thermally cracked stock.

³ A 100% cracked stock possessing the following inspections:

Gravity, ° API.....	26	Distillation:	
Aniline Point, ° F.....	165	20% at 620° F.	
Wt. percent Sulfur.....	1	80% at 720° F.	
Specific Dispersion.....	180	Percent off at 430° F.	

It is apparent from Table IV that diesel fuel oils can be effectively stabilized by the addition of an additive of the type described in the present invention. In general, the particular additive evaluated in Table IV is markedly successful in reducing the sediment-forming, color-degradation, and rusting tendencies of diesel fuels.

It will be noted that while the present invention is directed primarily toward fuel oils composed entirely of

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distillate hydrocarbon fractions, it also has application to fuel oils that contain small amounts of residual hydrocarbons. It is contemplated that the present invention would be effective in fuel oils containing up to 10% or more of residual hydrocarbons.

This application is a continuation-in-part of Serial No. 318,320, filed November 1, 1952, now abandoned.

What is claimed is:

1. A petroleum fuel oil composition of improved stability having a boiling point range between 300 and 700° F. and containing at least 10 volume percent of petroleum hydrocarbons derived from cracking operations and to which has been added

from 0.001 to 1.0 weight percent of a tertiary alkyl primary amine having 8 to 30 carbon atoms with a tertiary carbon atom attached directly to the amine group and from 0.001 to 0.5 weight percent of an oil soluble additive compound selected from the group consisting of:

(a) a phosphosulfurized hydrocarbon obtained by treating substantially olefin free lubricating oil bright stock having a viscosity of between 150 and 250 SSU at 210° F. with from 5 to 25 weight percent of a phosphorus sulfide at a temperature of from 375 to 475° F. to yield a phosphosulfurized hydrocarbon having a phosphorus content of from 2 to 6 weight percent, and

(b) lecithin, said fuel oil composition having improved storage stability characteristics when in contact with deleterious metals that induce instability by the formation of sediment.

2. A fuel oil composition as defined in claim 1 wherein said olefin free hydrocarbon is treated with from 10 to 20 weight percent of phosphorus sulfide at a temperature of from 400 to 430° F. for 1 to 20 hours.

3. A fuel oil composition as defined in claim 1 wherein said phosphosulfurized hydrocarbon is stabilized by the treatment of said phosphosulfurized hydrocarbon with from 0.1 to 5.0 weight percent of vinyl acetate at a temperature of from 60 to 400° F.

4. A fuel oil composition as defined by claim 1 wherein said tertiary alkyl primary amine contains from 12 to 15 carbon atoms and is employed at a concentration of from 0.005 to 0.2 weight percent.

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5. A fuel oil composition as defined in claim 1 wherein said composition has improved stability in contact with copper.

6. A petroleum fuel oil composition of improved stability having a boiling point range between 300 and 700° F. and containing at least 10 volume percent of petroleum hydrocarbons derived from cracking operations and to which has been added

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from 0.005 to 0.2 weight percent of a tertiary alkyl primary amine having 8 to 30 carbon atoms with a tertiary carbon atom attached directly to the amine group and from 0.001 to 0.05 weight percent of lecithin, whereby said fuel composition has improved storage stability characteristics when in contact with copper metals that induce instability by the formation of sediment.

7. A fuel oil composition as defined by claim 6 wherein said tertiary alkyl primary amine contains from 12 to 15 carbon atoms and is employed at a concentration of from 0.005 to 0.02 weight percent.

8. A petroleum fuel oil composition of improved stability having a boiling point range between 300 and 700° F. and containing at least 10 volume percent of petroleum hydrocarbons derived from cracking operations and to which has been added

from 0.005 to 0.2 weight percent of a tertiary alkyl primary amine having 12 to 15 carbon atoms with a tertiary carbon atom attached directly to the amine group and from 0.001 to 0.05 weight percent of an oil soluble phosphosulfurized hydrocarbon obtained by treating substantially olefin free lubricating oil

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bright stock having a viscosity of between 150 and 250 SSU at 210° F. with from 10 to 20 weight percent of a phosphorus sulfide at a temperature of from 400 to 430° F. for 1 to 20 hours to yield a phosphosulfurized hydrocarbon having a phosphorus content of from 2 to 6 weight percent and stabilizing said phosphosulfurized hydrocarbon with from 0.1 to 5.0 weight percent of vinyl acetate at a temperature of from 60 to 400° F., said fuel oil composition having improved storage stability characteristics when in contact with copper metals that induce instability by the formation of sediment.

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