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STABILIZED DISTILLATE HYDROCARBON FUEL OIL COMPOSITIONS AND ADDITIVES THEREFOR

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ABSTRACT OF THE DISCLOSURE

A stabilized distillate hydrocarbon fuel oil composition comprising a major proportion of a distillate hydrocarbon fuel and a minor proportion of a stabilizing additive comprised of (a) a polyamine having 2 to about 6 amino groups and containing about 24 to 50 carbons, (b) N,N'-disalicylidine-1,2-propylenediamine, and (c) a cyclohexylamine. The additives of the invention are useful in stabilizing distillate hydrocarbon fuels such as No. 2 fuel oils, diesel fuels, and jet fuels.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to stabilized petroleum distillate fuel oils and to additive compositions for stabilizing such fuel oils. More particularly, the invention is concerned with fuel oils such as diesel engine fuels, burner oils and jet fuels that are normally susceptible to deterioration with the formation of insoluble sludge and sediment, especially at elevated temperatures, which fuel oils have been stabilized to inhibit such deterioration; and to homogeneous liquid concentrates of a combination of additive compounds for so stabilizing such fuel oil, which concentrates are readily soluble in the fuel oils and which are unusually effective to so stabilize such fuel oils.

Description of the prior art

The prior art describes stabilized fuel oil compositions obtained by incorporating into the oils certain oil-soluble basic amino nitrogen-containing addition type copolymers. Such additives function primarily to suspend sludge and sediment that may already be present or that may form in their presence. While also somewhat effective as stabilizers, they are not entirely satisfactory for inhibiting the formation of colored bodies and insoluble matter, particularly at elevated temperatures. Diesel fuels having improved high temperature stability are expressly desired, for example, for use in locomotives wherein rather stringent pre-combustion conditions generally prevail. In jet fuels, which serve as heat exchange media for the engine before being combusted, high thermal stability is of prime importance.

Co-additives have been sought to augment the already satisfactory dispersancy obtainable with the polymeric additives and thereby to render fuel compositions less susceptible to the formation of normally occurring sludges and sediments that tend to clog fuel feed lines, spray nozzles, and filter screens. Substances proposed heretofore for use in conjunction with the polymeric dispersants, including certain long straight-chain and branched-chain

surface active amines, though providing some protection at ordinary ambient temperatures, are not entirely satisfactory stabilizers at elevated temperatures.

Another problem often encountered with fuel oils in the field is the development of objectionable haze under conditions of storage and transfer, apparently the result of water accumulation in the fuel.

It is an object of this invention to improve the stability of distillate hydrocarbon fuel oils agains deterioration such as the formation of discoloration, insoluble sludge and sediment. A specific object is to improve the stability of distillate hydrocarbon fuels by incorporating therein an inhibitor of fuel oil deterioration processes which is particularly effective at elevated temperatures as well as at ordinary temperatures and in which the combined additives function synergistically. Another object is to provide additive compositions for distillate hydrocarbon fuel oils, which compositions are homogeneous concentrates of a plurality of co-additives, and which concentrates are easily incorporated into said fuel oils and are unusually effective in inhibiting discoloration and the formation and deposition of insoluble sludge and sediment in such fuel oils, particularly at high temperatures. Other objects are to provide new compositions of matter. Still other objects will appear hereinafter.

It has been found that the above objects may be accomplished in accordance with this invention. Broadly, this invention comprises a distillate hydrocarbon fuel oil composition containing:

(a) a major proportion of a distillate hydrocarbon fuel;
(b) about 0.1 to about 5.0 pounds per thousand barrels of said distillate fuel oil composition of a polyamine having 2 to about 6 amino groups and containing about 24 to about 50 carbons;
(c) about 0.1 to about 5.0 pounds per thousand barrels of said distillate fuel oil composition of N,N'-disalicylidene-1,2-propylenediamine; and
(d) about 0.1 to about 5.0 pounds per thousand barrels of said distillate fuel oil composition of a cyclohexylamine selected from the group consisting of N,N-dimethylcyclohexylamine and dicyclohexylamine;

and an additive composition for distillate hydrocarbon fuel oils comprising:

(a) a polyamine having 2 to about 6 amino groups and containing about 24 to about 50 carbons;
(b) about 0.02 to about 50 parts per part of said polyamine of N,N'-disalicylidene-1,2-propylenediamine; and
(c) about 0.02 to about 50 parts per part of said polyamine of a cyclohexylamine selected from the group consisting of N,N-dimethylcyclohexylamine and dicyclohexylamine.

Distillate hydrocarbon fuel oil compositions containing the additives of this invention show remarkable stability, particularly at elevated temperatures, resulting in greatly reduced formation of insoluble material and colored bodies.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The stabilized distillate hydrocarbon fuel oil compositions of this invention are prepared by incorporating into a major proportion of a distillate hydrocarbon fuel an

additive comprising a polyamine having 2 to about 6 amino groups and containing about 24 to about 50 carbons, N,N'-disalicylidene-1,2-propylenediamine, and a cyclohexylamine selected from the group consisting of N,N-dimethylcyclohexylamine and dicyclohexylamine. Examples of the distillate hydrocarbon fuels that are stabilized by the incorporation therein of the additives of this invention are No. 2 fuel oil, diesel fuels, and jet fuels.

The polyamine component of the additive, as stated above, contains 2 to about 6 amino groups and about 24 to about 50 carbons. Preferably, the polyamine component contains 2 to about 4 amino groups and about 36 to about 42 carbons. Especially preferred polyamines are those derived from dimeric fatty acids which result from the controlled dimerization of unsaturated 18-carbon monocarboxylic fatty acids. Examples of particularly efficacious polyamines are those having the structures

$$H_2N—D—NH_2$$

hereinafter referred to as dimer diamine, and

$$H_2N—(CH_2)_3—NH—D—NH—(CH_2)_3—NH_2$$

hereinafter referred to as dimer tetramine. "D" is the 36-carbon hydrocarbon moiety derived from the dimerization of the unsaturated 18-carbon monocarboxylic fatty acid. The structure of D is not known with certainty. The concentration of polyamine in the distillate hydrocarbon fuel composition of this invention is about 0.1 to about 5.0, and preferably about 1.0 to about 3.0, pounds per thousand barrels (PTB) of said distillate hydrocarbon fuel composition.

The N,N'-disalicylidene-1,2-propylenediamine component of the additive is present in the distillate hydrocarbon fuel composition in a concentration of about 0.1 to about 5.0, and preferably about 1.0 to about 3.0, pounds per thousand barrels of said distillate hydrocarbon fuel composition.

As disclosed above, the cyclohexylamine component of the additive is selected from the group consisting of N,N-dimethylcyclohexylamine and dicyclohexylamine. The concentration of the cyclohexylamine in the distillate hydrocarbon fuel composition is about 0.1 to about 5.0, and preferably about 1.0 to about 3.0, pounds per thousand barrels of said distillate hydrocarbon fuel composition.

The components of the additive of this invention behave synergistically. Thus, the effect of the additive mixture on improving the stability of the distillate hydrocarbon fuel is greater than the sum of the individual contributions of the components.

In order to more clearly illustrate this invention, the following examples of preferred embodiments are presented.

EXAMPLE I

A series of No. 2 fuel oil compositions is prepared employing the additive components of this invention in combination according to the invention and individually for comparison to said No. 2 fuel oil compositions containing the combination of additives. The stability of each No. 2 fuel oil composition is determined as follows:

A sample of the filtered fuel oil composition is placed in an oxidation tube fitted with a sparger and a condenser and immersed in an oil bath heated at 180° F.±0.5° F. Filtered dry air at the rate of 5 liters per hour is passed through the sparger. The test is run for 192 hours. At the end of this time the sample is filtered to remove insoluble materials which are washed with filtered precipitation naphtha and dried in an oven at 210° F. The weight of the insoluble material is then determined and expressed as milligrams per hundred milliliters of fuel oil composition. The color of the fuel oil filtrate is determined by visual comparison with known standards according to the ASTM–D–1500 procedure. The results are based on a scale of 0.5 to 8.0 wherein increasing values indicate increasing darkness of the filtrate. The composition and the results of the stability test for each fuel oil composition is given in Table I.

TABLE I

Sample No.	Dimer tetramine, PTB	N,N-dimethylcyclohexylamine, PTB	N,N'-disalicylidene-1,2-propylenediamine, PTB	Insolubles, mg./100 ml.	ASTM-D-1500 color
1	1.0			4.03	4.5
2		1.0		1.88	3.5
3			1.0	3.06	<4.0
4	0.2	0.4	0.4	1.71	<3.5
5	3.0			3.14	<3.5
6		3.0		2.12	<3.5
7			3.0	2.46	3.5
8	1.0	1.0	1.0	1.09	2.5
9	1.0	1.0	0.5	2.06	3.0
10	1.0	0.5	1.0	1.52	<3.5
11	1.0	0.5	0.5	1.57	<3.5
12	0.5	1.0	1.0	1.97	3.0
13	0.5	0.5	1.0	2.51	3.0
14	0.5	1.0	0.5	1.80	3.0
15	0.5	0.5	0.5	2.03	3.0

The synergistic relationship of the components of the additives of this invention can be seen by comparing the stability of sample 4 to the stabilities of samples 1, 2, and 3. Each of the four fuel oil compositions contain 1.0 PTB of additive, but only sample 4 contains the mixed additive of the invention while each of the other three samples contains only one component of the mixed additive. Sample 4 has less insoluble material and lighter color than any of the other three samples. Similarly, sample 8 which contains the mixed additive of the invention at a concentration of 3.0 PTB has less insolubles and lighter color than samples 5, 6 and 7, each of which contains 3.0 PTB of only one component of the additive. In fact, a comparison of samples 9 through 15 to samples 5, 6 and 7 shows that the mixed additive of the invention at concentrations ranging down to 1.5 PTB compares favorably to samples containing 3.0 PTB of only one component of the additive mixture.

EXAMPLE II

Example I is repeated using a No. 2 fuel oil that is less stable than the No. 2 fuel oil used in Example I. The compositions of the No. 2 fuel oil compositions and their stabilities are given in Table II.

TABLE II

Sample No.	Dimer tetramine, PTB	Dimer diamine, PTB	N,N-dimethylcyclohexylamine, PTB	N,N'-disalicylidine-1,2-propylenediamine, PTB	Insolubles, mg./100 ml.	ASTM-D-1500 color
1	3.0				6.26	4.5
2		3.0			7.03	5.5
3			3.0		3.71	3.5
4				3.0	11.43	5.5
5	1.0		1.0	1.0	3.34	4.0
6		1.0	1.0	1.0	2.83	4.5
7	9.0				4.94	3.5
8		9.0			6.51	5.0
9			10.0		3.40	3.0
10				9.0	9.05	5.0
11	3.0		3.0	3.0	1.26	<3.0
12		3.0	3.0	3.0	1.12	3.0

The data illustrate the efficacy of both dimer tetramine and dimer diamine as the polyamine component in the additive mixture of the invention. A comparison of samples 5 and 6 to samples 1, 2, 3, and 4 and a comparison of samples 11 and 12 to samples 7, 8, 9, and 10 shows the synergism obtained at different concentrations by incorporating into a fuel oil the mixed stabilizing additives of the invention relative to the stability imparted to the same fuel oil by the aditive components individually.

EXAMPLE III

A series of jet fuel compositions is prepared using the additive components of the invention singly and in combination. The stabilities of the compositions are determined according to the procedure of Example I. Table III contains the compositions of the jet fuel compositions and the stabilities thereof.

TABLE III

Sample No.	Dimer-diamine, PTB	N,N-dimethyl-cyclohexyla-mine, PTB	Dicyclohexyl-amine, PTB	N,N'-disal-icylidine-1,2-propylene-diamine, PTB	Insol-ubles, mg./100 ml.	ASTM-D-1500 color
1	10.0				2.07	3.0
2		10.0			1.48	2.5
3			10.0		1.53	2.5
4				10.0	1.87	<3.0
5	0.1		5.0	5.0	0.96	2.0
6	5.0	5.0		0.1	1.13	2.5
7	5.0	0.1		5.0	1.02	<2.5
8	7.0				2.47	<3.5
9		7.0			1.86	3.0
10			7.0		1.95	<3.5
11				7.0	2.15	3.0
12	1.0		3.0	3.0	0.91	2.0
13	3.0		1.0	1.0	1.26	<2.5

The data illustrate the efficacy of the additive mixtures of this invention at various concentration levels and in various proportions of the constituents thereof as stabilizers for jet fuels.

EXAMPLE IV

A series of diesel fuel compositions is prepared using the additive components of the invention singly and in combination. The procedure of Example I is used to determine the stabilities of the compositions. The compositions and the stabilities of the diesel fuel compositions are given in Table IV.

TABLE IV

Sample No.	Dimer tetra-mine, PTB	N,N-di-methylcyclo-hexylamine, PTB	N,N'-di-salicylidine-1,2-propylene-diamine, PTB	Insol-ubles, mg./100 ml.	ASTM-D-1500 color
1	12.0			4.51	<3.5
2		12.0		3.14	<2.5
3			12.0	8.61	4.0
4	4.0	4.0	4.0	1.04	2.5
5	9.0			5.05	3.5
6		9.0		3.56	3.0
7			9.0	9.27	4.5
8	3.0	3.0	3.0	1.46	<3.0
9	6.0			5.46	4.0
10		6.0		3.60	3.5
11			6.0	9.84	5.0
12	2.0	2.0	2.0	2.81	3.5
13	3.0			5.98	<5.0
14		3.0		3.86	3.5
15			3.0	10.71	6.0
16	1.0	1.0	1.0	3.17	<4.0

The data illustrate the synergism of the additive mixtures of this invention at various concentration levels in imparting stability to diesel fuels.

It will be apparent that this invention provides distillate hydrocarbon fuel oils which are stabilized against objectionable deterioration by novel combinations of additives which, in combination, are unusually effective for such purposes. It will also be apparent that this invention provides novel additive compositions for distillate hydrocarbon fuel oils, which compositions are unusually effective for stabilizing distillate hydrocarbon fuel oils. It will be apparent, therefore, that this invention constitutes a valuable contribution to and advance in the art.

We claim:

1. A distillate hydrocarbon fuel oil composition comprising:
   (a) a major proportion of a distillate hydrocarbon fuel;
   (b) about 0.1 to about 5.0 pounds per thousand barrels of said distillate fuel oil composition of a polyamine selected from the group consisting of $H_2N—D—NH_2$ and $H_2N—(CH_2)_3—NH—D—NH—(CH_2)_3—NH_2$ wherein D is a 36-carbon hydrocarbon moiety derived from the controlled dimerization of unsaturated 18-carbon monocarboxylic fatty acids;
   (c) about 0.1 to about 5.0 pounds per thousand barrels of said distillate fuel oil composition of N,N'-disalicylidine-1,2-propylenediamine; and
   (d) about 0.1 to about 5.0 pounds per thousand barrels of said distillate fuel oil composition of a cyclohexylamine selected from the group consisting of N,N-dimethylcyclohexylamine and dicyclohexylamine.

2. The composition of claim 1 wherein the distillate hydrocarbon fuel oil is selected from the group consisting of No. 2 fuel oil, diesel fuel and jet fuel.

3. A distillate hydrocarbon fuel oil composition comprising:
   (a) a major proportion of a distillate hydrocarbon fuel;
   (b) about 1.0 to about 3.0 pounds per thousand barrels of said distillate fuel oil composition of a polyamine selected from the group consisting of $H_2N—D—NH_2$ and $H_2N—(CH_2)_3—NH—D—NH—(CH_2)_3—NH_2$ wherein D is a 36-carbon hydrocarbon moiety derived from the controlled dimerization of unsaturated 18-carbon monocarboxylic fatty acids;
   (c) about 1.0 to about 3.0 pounds per thousand barrels of said distillate fuel oil composition of N,N'-disalicylidene-1,2-propylenediamine; and
   (d) about 1.0 to about 3.0 pounds per thousand barrels of said distillate fuel oil composition of a cyclohexylamine selected from the group consisting of N,N-dimethylcyclohexylamine and dicyclohexylamine.

4. The composition of claim 3 wherein the distillate hydrocarbon fuel oil is selected from the group consisting of No. 2 fuel oil, diesel fuel and jet fuel.

5. An additive composition for distillate hydrocarbon fuel oils comprising:
   (a) a polyamine selected from the group consisting of $H_2N—D—NH_2$ and $H_2N—(CH_2)_3—NH—D—NH—(CH_2)_3—NH_2$ wherein D is a 36-carbon hydrocarbon moiety derived from the controlled dimerization of unsaturated 18-carbon monocarboxylic fatty acids;
   (b) about 0.02 to about 50 parts per part of said polyamine of N,N'-disalicylidene-1,2-propylenediamine; and
   (c) about 0.02 to about 50 parts per part of said polyamine of a cyclohexylamine selected from the group consisting of N,N-dimethylcyclohexylamine and dicyclohexylamine.

6. An additive composition for distillate hydrocarbon fuel oils comprising:

(a) a polyamine selected from the group consisting of $H_2N—D—NH_2$ and $H_2N—(CH_2)_3—NH—D—NH—(CH_2)_3—NH_2$ wherein D is a 36-carbon hydrocarbon moiety derived from the controlled dimerization of unsaturated 18-carbon monocarboxylic fatty acids;

(b) about 0.33 to about 3.0 parts per part of said polyamine of N,N'-disalicylidene-1,2-propylenediamine; and

(c) about 0.33 to about 3.0 parts per part of said polyamine of a cyclohexylamine selected from the group consisting of N,N-dimethylcyclohexylamine and dicyclohexylamine.

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