United States Patent

Rakow et al.

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[45] **Feb. 8, 1972**

[54] **STABILIZED DISTILLATE HYDROCARBON FUEL OIL COMPOSITIONS AND ADDITIVES THEREFOR**

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[52] **U.S. Cl.** **44/63,** 44/66, 44/71, 44/73, 44/74, 252/403

[51] **Int. Cl.** **C01l 1/18,** C01l 1/22

[58] **Field of Search** 44/63, 66, 71, 73, 74; 252/403

[56] **References Cited**

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Attorney—J. Richard German

[57] **ABSTRACT**

A stabilized distillate hydrocarbon fuel oil composition comprising a major proportion of a distillate hydrocarbon fuel and a minor proportion of a stabilizer comprising (a) an additive selected from the group consisting of (1) an amide plus a Schiff base; (2) an amide containing a Schiff base group; and (3) an amide containing a Schiff base group in combination with either an amide or a Schiff base; and (b) 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.

5 Claims, No Drawings

STABILIZED DISTILLATE HYDROCARBON FUEL OIL COMPOSITIONS AND ADDITIVES THEREFOR

BACKGROUND OF THE INVENTION

1. 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.

2. 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 precombustion 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.

Coadditives 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 feedlines, 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 against 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 coadditives, 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 oil and
b. a minor proportion of a stabilizer comprising:
1. an additive selected from the group consisting of:
a. an amide plus a Schiff base;
b. an amide containing a Schiff base group; and
c. an amide containing a Schiff base group in combination with either an amide or a Schiff base; and

2. a cyclohexylamine selected from the group consisting of N,N-dimethylcyclohexylamine and dicyclohexylamine;

and a stabilizer composition for distillate hydrocarbon fuel oils comprising:

a. an additive selected from the group consisting of:
1. an amide plus a Schiff base;
2. an amide containing a Schiff base group; and
3. an amide containing a Schiff base group in combination with either an amide or a Schiff base; and
b. a cyclohexylamine selected from the group consisting of N,N-dimethylcyclohexylamine and dicyclohexylamine.

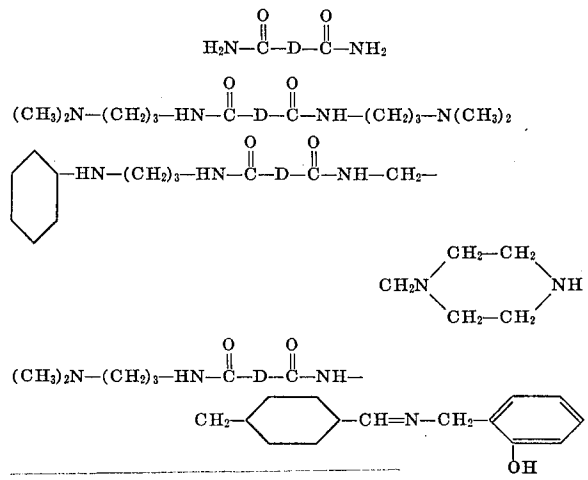
Distillate hydrocarbon fuel oil compositions containing the additives of this invention show remarkable stability, particularly at elevated temperatures, resulting in greatly reduced formation of insoluble material and colored bodies.

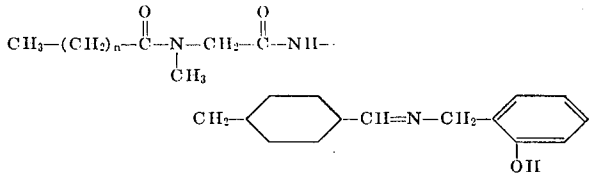
DESCRIPTION OF THE PREFERRED EMBODIMENTS

The stabilized distillate hydrocarbon fuel oil compositions of this invention are prepared by incorporating into a major proportion of a distillate hydrocarbon fuel oil a stabilizer comprising an additive selected from the group consisting of an amide and a Schiff base, an amide containing a Schiff base group, and an amide containing a Schiff base group in combination with either an amide or a Schiff base; and a cyclohexylamine selected from the group consisting of N,N-dimethylcyclohexylamine and dicyclohexylamine. Examples of the distillate hydrocarbon fuel oils that are stabilized by the incorporation therein of the additive of this invention are No. 2 fuel oil, diesel fuels, and jet fuels.

The additive component of the stabilizer, as stated above, is selected from the group consisting of an amide and a Schiff base, an amide containing a Schiff base group, and an amide containing a Schiff base group in combination with either an amide or a Schiff base. Thus, the additive component may be a mixture of an amide and a Schiff base, it may be a single compound containing both an amide group and a Schiff base group, it may be a mixture of an amide and a single compound containing both an amide group and a Schiff base group, or it may be a mixture of a Schiff base and a single compound containing both an amide group and a Schiff base group.

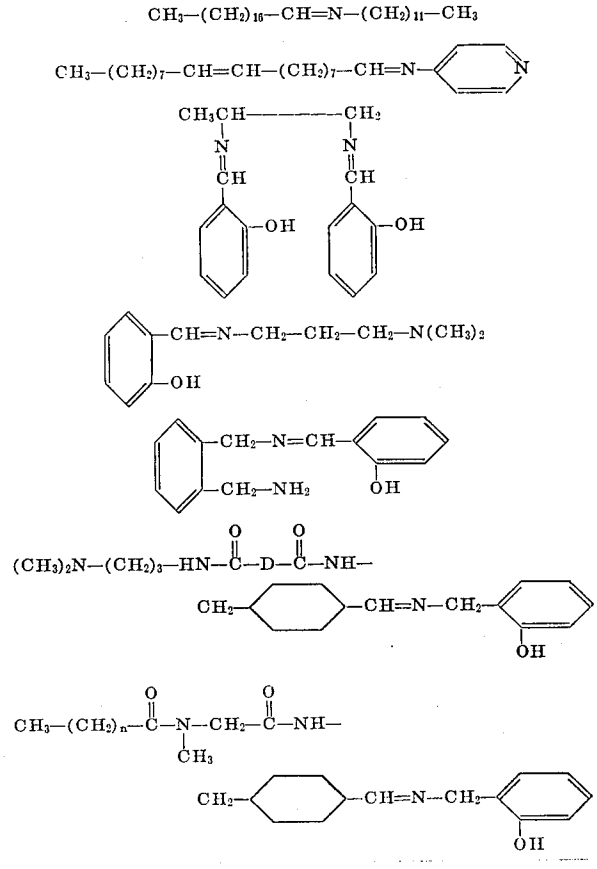
The amide may be aromatic, saturated or unsaturated aliphatic, naphthenic, or contain a combination of these hydrocarbyl moieties. It may contain one, two or more amide groups. It may also contain other functional groups such as amino groups, hydroxyl groups, Schiff base groups, and heterocycle groups. Examples of suitable amides are stearamide, oleamide, acetanilide, benzamide, adipamide, polyamides derived from the condensation of polymerized fatty acids with polyalkyl polyamines, and amides having the structures:





where *n* is 10 to 20 and D is the 34-carbon noncarboxyl portion of a dicarboxylic acid produced by the controlled dimerization of unsaturated C_{18} monocarboxylic fatty acids. The structure of D is not known with certainty.

The Schiff base may be aromatic, saturated or unsaturated aliphatic, naphthenic, or contain a combination of these hydrocarbyl moieties. It may contain one, two or more Schiff base groups and it may also contain other functional groups such as amino groups, hydroxyl groups, amide groups, and heterocycle groups. Examples of suitable Schiff bases are those having the structures:



wherein *n* and D are the same as set forth above for amides.

The concentrations of the components of the stabilizer in the distillate hydrocarbon fuel oil composition of this invention will vary depending on, among other things, the tendency of the hydrocarbon fuel oil to undergo deterioration. While from the disclosure of this invention it would be within the capability of those skilled in the art to find by simple experimentation the optimum concentrations for any particular hydrocarbon fuel oil, generally about 0.5 to about 20.0, and preferably about 1.0 to about 10.0, pounds of each component per thousand barrels (PTB) of distillate hydrocarbon fuel oil composition is used. Thus the concentration of the additive component of the stabilizer in the distillate hydrocarbon fuel oil composition of this invention is about 0.5 to about 20.0, and preferably about 1.0 to about 10.0, pounds per thousand barrels (PTB) of said distillate hydrocarbon fuel oil composition when the additive component is a single compound containing both an amide group and a Schiff base group. In the case where the additive component is a two-constituent mixture, i.e., a mixture of an amide and a Schiff base, a mixture of an amide and a single compound containing both an amide group and a Schiff base group, or a mixture of a Schiff base and a single compound containing both an amide group and a Schiff base group, about 0.5 to about 20.0, and preferably about 1.0 to about 10.0, pounds of each constituent of the additive component per thousand barrels of distillate hydrocarbon fuel oil composition is used.

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 oil composition is about 0.5 to about 20.0, and preferably about 1.0 to about 10.0, pounds per thousand barrels (PTB) of said distillate hydrocarbon fuel oil composition.

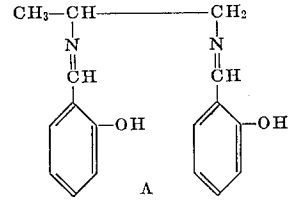
The components of the stabilizer of this invention behave synergistically. Thus, the effect of the stabilizer mixture on improving the stability of the distillate hydrocarbon fuel oil is greater than the sum of the individual contributions of the components.

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

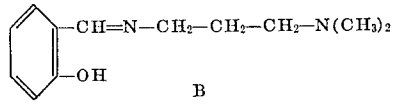
EXAMPLE I

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

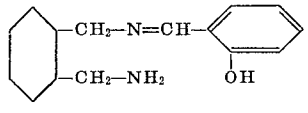
A sample of the filtered fuel oil composition is placed in an oxidation tube fitted with a sparger and a condenser and immersed in an oil bath heated at 180° F. ±0.5° F. Filtered dry air at the rate of 5 liters per hour is passed through the sparger. The test is run for 192 hours. At the end of this 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 following compounds are used in the No. 2 fuel oil compositions:



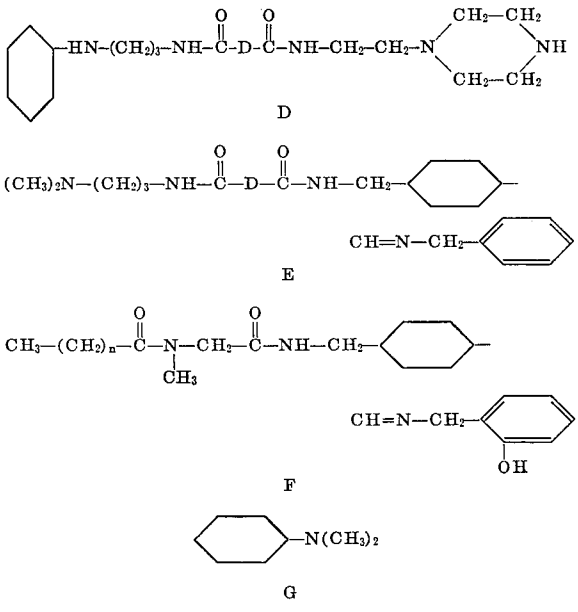
A



B



C



wherein *n* and D are as set forth above. The composition and the results of the stability test for each fuel oil composition are given in Table I. In the table, each compound is represented by its letter designation as shown above.

TABLE I

Composition number	Compound	Concentration, ptb.	Insolubles, mg./100 ml.	ASTM-D-1500 color
1	A	9.0	9.05	5.0
2	B	10.0	3.54	3.5
3	C	10.0	7.17	5.5
4	D	8.0	5.66	5.0
5	E	8.0	7.20	5.0
6	F	8.0	7.57	5.0
7	G	3.0	3.71	3.5
8	G	10.0	3.40	3.0
9	D+A+G	3.0+3.0+3.0	3.40	3.5
10	E+A+G	3.0+3.0+3.0	2.60	3.0
11	F+A+G	3.0+3.0+3.0	1.77	3.0
12	D+C+G	3.0+3.0+3.0	3.29	3.5
13	F+C+G	3.0+3.0+3.0	3.05	3.5
14	D+B+G	3.0+3.0+3.0	1.77	3.0
15	F+B+G	3.0+3.0+3.0	2.37	3.0

The data show that the compositions numbered 9 through 15, i.e., those that contain the stabilizer mixture of the invention, have insolubles at levels which are as low as, and which are generally markedly lower than, compositions containing individual components of the stabilizer mixture at comparable levels. The colors of compositions 9 through 15 compare favorably to compositions 1 through 8, i.e., those containing individual components of the stabilizer mixture, being generally as light and often considerably lighter in color.

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 amide components of the stabilizers are polyamides derived from the condensation of polymerized fatty acids with polyalkyl polyamines. The polyamides are marketed by Emery Industries, Inc. under the tradenames Emerez 1500, Emerez 1502, and Emerez 1514. The Schiff base component is N,N'-disalicylidine-1,2-propylenediamine denoted as A in Example I and here. The cyclohexylamine component is N,N-dimethylcyclohexylamine denoted as G in Example I and here. The compositions of the No. 2 fuel oil compositions and their stabilities are given in Table II.

TABLE II

Composition number	Compound	Concentration, ptb.	Insolubles, mg./100 ml.	ASTM-D-1500 color
1	A	9.0	9.38	5.5
2	G	9.0	7.45	4.0
3	Emerez 1500	9.0	38.77	6.5
4	Emerez 1502	9.0	12.43	5.5
5	Emerez 1514	9.0	9.46	5.0
6	Emerez 1500	3.0	4.08	3.5
	A	3.0		
	G	3.0		
7	Emerez 1502	3.0	3.86	3.0
	A	3.0		
	G	3.0		
8	Emerez 1514	3.0	3.60	3.0
	A	3.0		
	G	3.0		

The data in Table II show that compositions 6, 7, and 8, i.e., these that contain the stabilizer mixture of the invention, have much lower levels of insolubles and lighter colors than do compositions 1 through 5, i.e., compositions containing individual components of the stabilizer mixture at comparable levels.

EXAMPLE III

A series of diesel fuel compositions is prepared using the components of the stabilizer in combination according to the invention and singly for comparison purposes. The stabilities of the compositions are determined according to the procedure of Example I. The composition and the results of the stability test for each diesel fuel composition are given in Table III. In the table, each compound is represented by its letter designation as set forth in Example I. In addition to the compounds disclosed in Example I, dicyclohexylamine which is designated H is used in some of the compositions.

TABLE III

Composition number	Compound	Concentration, ptb.	Insolubles, mg./100 ml.	ASTM-D-1500 color
1	B	1.5	4.31	4.5
2	D	1.5	7.23	6.0
3	H	1.5	4.02	4.0
4	B+D+H	0.5+0.5+0.5	3.87	<4.0
5	C	3.0	8.27	6.5
6	E	3.0	8.34	6.5
7	H	3.0	3.95	3.5
8	C+E+H	1.0+1.0+1.0	3.68	3.0
9	E+H	2.0+1.0	3.75	<3.5
10	A	15.0	8.49	<4.0
11	F	15.0	5.98	3.5
12	G	15.0	3.02	2.5
13	A+F+G	5.0+5.0+5.0	1.53	<2.5
14	F+G	5.0+5.0	1.80	<2.5

The data in Table III show that the compositions prepared in accordance with the invention, i.e., compositions 4, 8, 9, 13, and 14, have lower levels of insolubles and lighter colors than do compositions containing individual components of the stabilizer at comparable levels.

EXAMPLE IV

A series of jet fuel compositions is prepared using the components of the stabilizer singly and in combination according to the invention. The procedure of Example I is used to determine the stabilities of the compositions. Table IV contains the compositions and the stabilities of the jet fuel compositions. Each compound is represented by its letter designation as set forth in Example I.

TABLE IV

Composition number	Compound	Concentration, ptb.	Insolubles, mg./100 ml.	ASTM-D-1500 color
1	B	1.5	3.46	<4.0
2	E	1.5	7.62	6.0
3	G	1.5	3.17	3.5
4	B+E+G	0.5+0.5+0.5	2.98	<3.5
5	D	9.0	4.77	4.0
6	E	9.0	5.83	4.0
7	H	9.0	3.07	<3.0
8	D+E+H	3.0+3.0+3.0	2.56	2.5
9	C	12.0	5.76	4.0
10	D	12.0	4.31	3.5
11	G	12.0	2.87	2.5
12	C+D+G	4.0+4.0+4.0	1.46	2.0

The data in Table IV show that compositions 4, 8, and 12 which contain the mixed stabilizers of the invention have less insoluble material and are lighter in color than compositions containing individual components of the stabilizer at comparable levels.

EXAMPLE V

Example I is repeated using the No. 2 fuel oil of Example II. The stabilities of the fuel oil compositions are determined according to the procedure outlined in Example I. The compositions and the stabilities of the fuel oil compositions are given in Table V. Each compound is represented by its letter designation as set forth in Example I.

TABLE V

Composition number	Compound	Concentration, ptb.	Insolubles, mg./100 ml.	ASTM-D-1500 color
1	A	30.0	8.12	<5.0
2	C	30.0	6.84	5.0
3	G	30.0	6.32	3.5
4	A+C+G	10.0+10.0+10.0	3.71	3.0
5	A	45.0	7.46	4.5
6	C	45.0	6.03	4.5
7	G	45.0	5.64	3.0
8	A+C+G	15.0+15.0+15.0	2.93	<3.0
9	A	60.0	6.74	<3.5
10	C	60.0	5.47	3.5
11	G	60.0	4.86	2.5
12	A+C+G	20.0+20.0+20.0	2.56	2.0

The data in Table V show that the fuel oil compositions containing the stabilizer mixtures of the invention, i.e., compositions 4, 8, and 12, have lower levels of insolubles and lighter colors than do compositions containing individual components of the stabilizer mixture at comparable levels.

EXAMPLE VI

A series of No. 2 fuel oil compositions is prepared using the components of the stabilizer singly and in various combinations according to the instant invention. The stabilities of the fuel oil compositions are determined according to the procedure outlined in Example I. Each component compound is represented by its letter designation as set forth in Example I. The compositions and the stabilities of the fuel oil compositions are given in Table VI.

TABLE VI

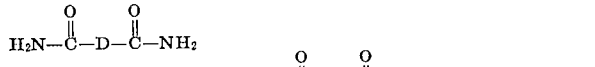
Composition number	Compound	Concentration, ptb.	Insolubles, mg./100 ml.	ASTM-D-1500 color
1	A	9.0	5.26	<5.5
2	G	9.0	3.60	4.0
3	E	9.0	7.83	5.5
4	F	9.0	9.72	6.0
5	A+G+E	3.0+3.0+3.0	2.77	4.0
6	A+G+E	3.0+3.0+3.0	1.94	4.0
7	G+E	3.0+3.0	3.03	<4.5
8	G+F	3.0+3.0	2.97	4.0

The data in Table VI show that compositions 5, 6, 7, and 8, i.e., those containing the stabilizer mixtures of the invention, have lower levels of insolubles and colors generally as good as those compositions containing individual components at comparable levels. In fact, compositions 7 and 8 contain stabilizers comprised of a cyclohexylamine and a compound containing both amide and Schiff base groups at overall levels less than those of the individual components, i.e., compositions 1, 2, 3, and 4, and have lower levels of insolubles and colors generally as light as those of compounds 1, 2, 3, and 4.

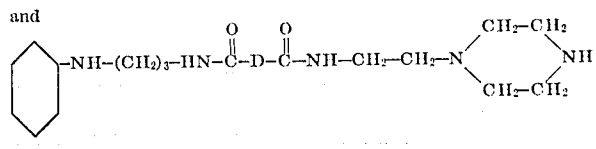
It is obvious that many variations can be made in the compositions set forth above without departing from the spirit and scope of our invention.

We claim:

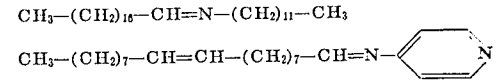
1. A distillate hydrocarbon fuel oil composition comprising:
   a. a major proportion of a distillate hydrocarbon fuel oil and
   b. a minor proportion of a stabilizer comprising:
      1. an additive selected from the group consisting of:
         a. an amide plus a Schiff base;
         b. an amide containing a Schiff base group; and
         c. an amide containing a Schiff base group in combination with either an amide or a Schiff base wherein the amide of (a) and (c) is selected from the group consisting of polyamides derived from the condensation of polymerized fatty acids with polyalkyl polyamines and amides having the structures

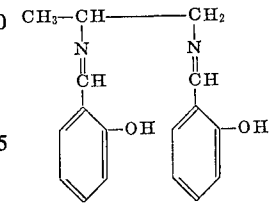


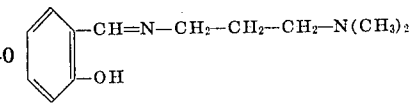
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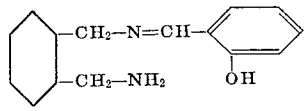
wherein D is the 34-carbon noncarboxyl portion of a dicarboxylic acid produced by the controlled dimerization of unsaturated C_{18} monocarboxylic fatty acids, the Schiff base of (a) and (c) is selected from the group consisting of Schiff bases having the structures



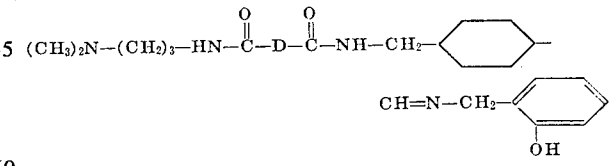




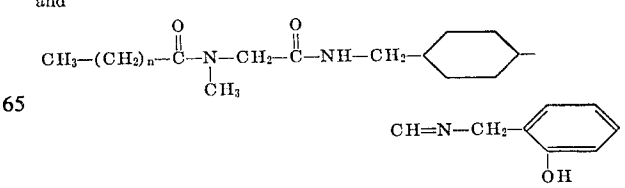
and



and the amide containing a Schiff base group of (b) and (c) is selected from the group of compounds having the structures



and



wherein n is 10 to 20 and D is the 34-carbon noncarboxyl portion of a dicarboxylic acid produced by the controlled dimerization of unsaturated C_{18} monocarboxylic fatty acids; and

2. a cyclohexylamine selected from the group consisting of N,N-dimethylcyclohexylamine and dicyclohex-

ylamine, wherein each component of the stabilizer is present in the hydrocarbon fuel oil composition in the amount of about 0.5 to about 20.0 pounds per thousand barrels of said hydrocarbon fuel oil composition.

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.

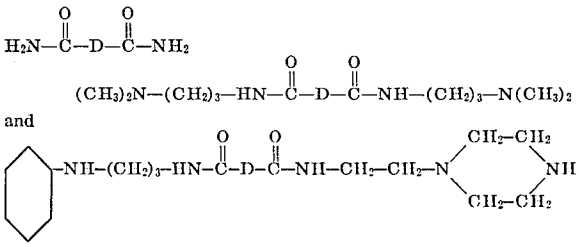
3. The composition of claim 1 wherein each component of the stabilizer is present in the hydrocarbon fuel oil composition in the amount of about 1.0 to about 10.0 pounds per thousand barrels of said hydrocarbon fuel oil composition.

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. A stabilizer composition for distillate hydrocarbon fuel oils comprising:

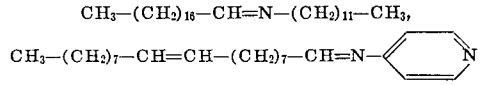
a. an additive selected from the group consisting of:

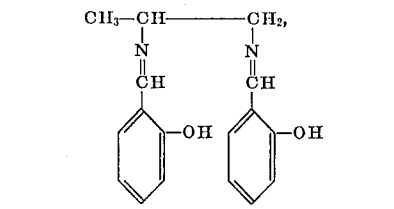
1. an amide plus a Schiff base;
2. an amide containing a Schiff base group; and
3. an amide containing a Schiff base group in combination with either an amide or a Schiff base wherein the amide of (1) and (3) is selected from the group consisting of polyamides derived from the condensation of polymerized fatty acids with polyalkyl polyamines and amides having the structures

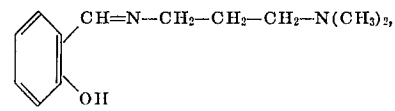


and

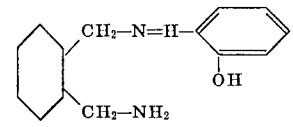
wherein D is the 34-carbon noncarboxyl portion of a dicarboxylic acid produced by the controlled dimerization of unsaturated C_{18} monocarboxylic fatty acids, the Schiff base of (1) and (3) is selected from the group consisting of Schiff bases having the structures



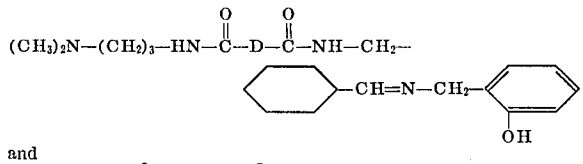




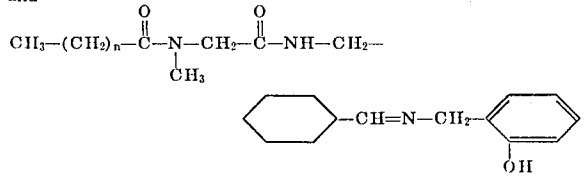
and



and the amide containing a Schiff base group of (2) and of (3) is selected from the group of compounds having the structures



and



wherein n is 10 to 20 and D is the 34-carbon noncarboxyl portion of a dicarboxylic acid produced by the controlled dimerization of unsaturated C_{18} monocarboxylic fatty acids; and

b. a cyclohexylamine selected from the group consisting of N,N-dimethylcyclohexylamine and dicyclohexylamine, wherein the weight ratio of each constituent of the additive component to the cyclohexylamine is from about 1:40 to about 40:1.

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