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3,092,475

FUEL COMPOSITION

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The present invention relates to fuel oil compositions stabilized against the harmful effects of oxidation or deterioration. More particularly the invention is concerned with distillate fuel oils containing certain additives adapted to stabilize the fuel oils against oxidative deterioration during storage or use.

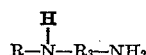
Hydrocarbon fuels, for example, those distilling primarily in the range from about 300 to 750° F., tend to deteriorate and form sediment, insoluble gum, etc. which if not removed, plug filter screens, orifices and other parts of equipment used in burning the oils. The formation of sediment, insoluble gum, etc. in these oils is attributable primarily to the oxidation of unstable constituents contained in the oils. This oxidation takes place under prolonged storage at atmospheric temperatures as well as under elevated temperatures during use.

It has been found that certain oil-compatible, i.e. soluble, miscible or dispersible, oxyalkylated fatty diamines when added in relatively small amounts to distillate fuel oils effectively stabilize the oil against deterioration. The oxyalkylated fatty diamines of the present invention are prepared by reacting about 5 to 80 weight percent, preferably about 30 to 70 weight percent of a C₂-C₄ alkylene oxide, for instance, ethylene oxide and propylene oxide or mixtures thereof with about 20 to 95 weight percent, preferably about 70 to 30 weight percent of certain fatty diamines. These percentages are based on the total amount of diamine and alkylene oxide. The amount of alkylene oxide employed can be varied to obtain a product of maximum efficiency for the particular fuel oil utilized. Mixtures of alkylene oxides, as aforementioned, can also be employed and in fact have been found to improve the solubility characteristics of the finished product. If utilized, mixtures of ethylene oxide and propylene oxide are preferred, generally in a ratio of about 0.5 to 5 parts ethylene oxide to 1 part propylene oxide.

The oxyalkylation reaction can in general be conducted at temperatures of about 250° F. to 400° F., preferably about 300° F. to 375° F. and, if desired, in the presence of an oxyalkylation catalyst in catalytic amounts. Examples of suitable oxyalkylation catalysts that may be employed are sodium methylate, sulfuric acid, sulfonic acids, etc. Prior to oxyalkylation, it is generally found desirable to dissolve the fatty diamines of the present invention in an aromatic hydrocarbon solvent such as xylene. Upon completion of the oxyalkylation the solvent can be removed and the finished product added as such to the fuel oils of the present invention or it can be added in its diluted form. In the latter case, the oxyalkylated base will generally range from about 60 to 95 percent by weight depending on the amount of solvent employed. If desired, the oxyalkylated base-xylene product can be further diluted, as for example, to where it has 50% or less of active ingredient.

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The fatty diamine contemplated by the present invention has the structural formula:



in which R is an aliphatic hydrocarbon radical of at least about 6 and preferably about 12 to 22 carbon atoms and R₃ is a divalent aliphatic hydrocarbon radical containing about 2 to 8 carbon atoms. The hydrocarbon radicals can be straight or branched chain and substituted or unsubstituted. Preferably, R₃ is a polymethylene group of about 2 to 8 carbon atoms and advantageously about 2 to 4 carbon atoms. These diamines can be prepared by a variety of well-known procedures, as for example, by reacting an aliphatic chloride containing the desired number of carbon atoms with a polymethylene diamine which contains from about 2 to 8 methylene groups. The aliphatic R group which is attached to the nitrogen atom is either saturated or unsaturated and is preferably an alkyl or alkylene residue radical obtained from fatty acids. Fatty acids which are suitable for providing residues containing the desired number of carbon atoms can be obtained from fats and oils such as soybean oil, lard oil, castor oil, corn oil, tallow, coconut oil, etc. or from resin acids such as those derived from tall oil which contains a mixture of fatty acids and resin acids.

An example of a preferred fatty amine used in the preparation of the oxyalkylated products of this invention is a diamine designated as "Duomeen T" in which R₃ in the above formula is trimethylene and R is the straight chain hydrocarbon residue derived from tallow fatty acids containing 16 to 18 carbon atoms, both saturated and unsaturated. Similar fatty diamines can be used in which the hydrocarbon group is derived from monobasic acids such as, for example, lauric acid, myristic acid, palmitic acid, stearic acid, margaric acid, oleic acid, ricinoleic acid, linoleic acid, etc., as well as monobasic acids derived by oxidation of petroleum waxes.

The fuel oils which are improved in accordance with this invention are hydrocarbon fractions boiling primarily in the range from about 300° F. to 750° F. Such fuel oils are generally known as distillate fuel oils. It must be understood, however, that this term is not restricted to straight-run distillates. These fuels can be straight-run distillate fuel oils, catalytically or thermally cracked distillate fuel oils or mixtures of straight-run distillate fuel oils, naphthas and the like, with cracked distillate stocks. The cracked materials will frequently be about 15 to 70 volume percent of the fuel. 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.

In order to effectively stabilize the distillate fuel oils the condensation products of the present invention are added to the fuel oils in concentrations varying between about 5 pounds per thousand barrels of oil and about 250 pounds per thousand barrels of oil. Preferably the concentration varies between about 5 and 50 pounds per thousand barrels of oil.

Metal deactivators in relatively small amounts, i.e. up to about 2 pounds/1000 barrels of fuel oil, preferably about .5 to 1 pound per 1000 barrels of fuel oil, can be added along with the additives of the present invention to enhance the latter's stabilizing effect on the fuel oils. Examples of suitable metal deactivators are N,N'-disalicylidene-1,2-propylene diamine, dimethyldithio oxamide, condensated products of O-hydroxy aromatic aldehyde or O-hydroxy aromatic ketone and an aliphatic polyamine as disclosed by Downing et al. in Patents Nos. 2,181,121; 2,255,597 and 2,301,861. If desired, the fuel oil compositions of the present invention can contain other additives for the purpose of achieving other results. Thus, for example, there can be present foam inhibitors, anti-rust agents, and ignition and burning quality improvers.

The tests used to determine the stability of the fuel oil compositions of the present invention were the 100° F. cabinet storage test and the high temperature stability test. In the 100° F. cabinet storage test 400 milliliter samples of the fuel oil composition are placed in a cabinet maintained at 100° F., for periods of 2, 4 and 6 months. At the end of the test periods the sample is removed from the cabinet and cooled. The cooled sample is filtered to remove the insoluble matter. The weight of such matter in milligrams is reported as the amount of deposit or sediment per 100 milliliters.

In the high temperature stability test, samples of the fuel oil compositions are passed through a filter disc immediately after preparation ("0 week storage"), and again after storage in cans at room temperature ("12 weeks' storage"). In addition, the fuel compositions are similarly tested without heating to show deterioration at room temperature ("before heating"), and in the regular high temperature test at 300° F. for 90 minutes ("after heating"). The color of the filtered oil is recorded and the condition of each filter disc after the test is given a numerical scale rating, 0 representing no staining and 5 representing heavy staining and deposits.

The following examples will serve to illustrate the compositions of the present invention but are not to be considered limiting.

EXAMPLE I

127 grams of "Duomeen T" were dissolved in 85 grams of xylene. This solution was oxyalkylated with 84 grams of ethylene oxide using 0.30 weight percent of sodium methylate as the catalyst at a reaction temperature of 300 to 350° F. The reaction was continued at least until the product is substantially completely dehydrated. This yielded a product which was 71.5% active and contained 40% ethylene oxide on an active ingredient basis. The oxyalkylated base was further diluted with xylene to 50%

active ingredient content and designated as SS-1102C. Using the above method, product SS-1102A containing 10% ethylene oxide and product SS-1102E containing 70% ethylene oxide were also prepared as shown on Table III.

The above oxyalkylated products were added in various concentrations to a distillate fuel oil composed of 50 volume percent water white distillate having an end point of 565 and 50 volume percent light cycle oil derived by catalytic cracking of gas oil. The physical properties of the fuel oil and its constituents are shown in Table I.

Table I

TESTS ON NEAT FUEL

Composition:		
565 E.P. water white distillate	-----	50
Fluid light cycle oil	-----	50
Physical tests:		
Gravity, ° API	-----	34.4
Flash, ° F	-----	170
Cloud point, ° F	-----	-18
Pour Point, ° F	-----	-30
Distillation (200 ml.), ° F.:		
I.B.P.	-----	354
5%	-----	419
10%	-----	442
20%	-----	456
30%	-----	464
40%	-----	472
50%	-----	480
60%	-----	488
70%	-----	498
80%	-----	508
90%	-----	524
95%	-----	536
E.P.	-----	563
Recovery percent	-----	99.5
Residue percent	-----	0.5

The fuel compositions thus prepared were subjected to the 100° F. cabinet storage test for periods of two and four months, respectively, to determine the effect of the additive contained therein for stabilizing heating oils. The fuel compositions were also subjected to the high temperature stability test to determine the effectiveness of the additives as stabilizers for diesel fuels. The neat fuel was similarly tested for purposes of comparison. The test results are shown in Table II.

Table II

100° F. CABINET STORAGE TEST

Additive	Dosage #/MB	MDA #/MB	Two months			Four months		
			Deposits mgs./100 ml.	Color NPA	Visual Inspection for precipitate in storage tube	Deposits mgs./100 ml.	Color NPA	Visual Inspection for precipitate in storage tube
Neat fuel			2.2	3-	Heavy	3.4	3	Heavy.
(1) SS-1102A (amine plus 10% ethylene oxide)	24		0.5	3½-	None	0.7	3½-	None.
(2) SS-1102C (amine plus 40% ethylene oxide)	30		0.5	3½-	do	0.8	3½-	Do.
(3) SS-1102E (amine plus 70% ethylene oxide)	40		1.1	3-	Trace	1.0	3½-	Trace.
(4) SS-1102A (amine plus 10% ethylene oxide)	48		0.7	3½-	None	0.3	3½+	None.
(5) SS-1102C (amine plus 40% ethylene oxide)	60		1.4	3½-	do	1.2	3½-	Medium.
(6) SS-1102E (amine plus 70% ethylene oxide)	80		1.0	3-	do	0.9	3½-	None.
(7) SS-1102A (amine plus 10% ethylene oxide)	24	1	0.4	3+	do	0.5	3½-	Do.
(8) SS-1102C (amine plus 40% ethylene oxide)	30	1	1.0	3-	do	0.8	3½-	Do.
(9) SS-1102E (amine plus 70% ethylene oxide)	40	1	0.8	3+	Trace	0.9	3½-	Trace.

See footnote at end of table.

Table II—Continued
HIGH TEMPERATURE STABILITY TEST

Additive	MDA #/MB	0 week's storage						12 weeks' storage					
		Before heating			After heating			Before heating			After heating		
		Filter disc ¹	Color		Filter disc ¹	Color		Filter disc ¹	Color		Filter disc ¹	Color	
			NPA	OD		NPA	OD		NPA	OD		NPA	OD
Neat fuel		2	2+	11	4	4+	86	3	2-	19	4	4½	100
(1) SS-1102A (amine plus 10% ethylene oxide)		0	2	10	4	4+	65	1	3-	20	3	4½	70
(2) SS-1102C (amine plus 40% ethylene oxide)		0	2	9	4	4+	68	0	3-	18	3	4½+	88
(3) SS-1102E (amine plus 70% ethylene oxide)		0	2	9	4	4½	68	0	3-	18	3-4	4½+	100
(4) SS-1102A (amine plus 10% ethylene oxide)		0	2-	10	2	4-	41	1	3-	20	2	4½	61
(5) SS-1102C (amine plus 40% ethylene oxide)		0	2-	9	2	4-	56	0	3-	18	1	4½-	58
(6) SS-1102E (amine plus 70% ethylene oxide)		0	2	9	3	4+	49	0	3-	18	2	4½	76
(7) SS-1102A (amine plus 10% ethylene oxide)	1	0	2	9	0	3-	17	1	3	22	3	4½	76
(8) SS-1102C (amine plus 40% ethylene oxide)	1	0	2	9	0	2½+	18	0	3	22	1	4-	42
(9) SS-1102E (amine plus 70% ethylene oxide)	1	1	1+	10	1	3-	19	2	3-	22	3	4½	75

¹ Filter disc code: 0—no discoloration; 1—light discoloration but no definite evidence of precipitate; 2—medium brown discoloration but not black, indication of trace of precipitate; 3—black deposit showing definite evidence of insolubles in fuel; 4—black deposit showing considerable precipitate; 5—black deposit showing heavy precipitate.

The results of the 100° F. cabinet storage test of Table II show that although the oxyalkylated product additives of the present invention did not improve color they effectively inhibited the formation of deposits in the fuel oil. For example, comparing the tests on the fuel compositions with the test on the neat fuel, it is seen that the amount of deposit formed in the neat fuel was at the lowest 2.2 milligrams per 100 milliliters whereas the amount of deposit formed in the novel fuel compositions was at the highest 1.4. In the majority of cases the amount of deposit formed in the additive compositions was below 1.0 milligram per 100 milliliters and as low as 0.5 milligram per 100 milliliters. Visual inspection of the storage tubes after 4 months showed only trace amounts of deposit when using SS-1102E and none with the other additives as compared to a heavy precipitate in the neat fuel tube. Also shown in Table II is the general enhancement of the additives of Example I as a fuel oil stabilizer by the incorpora-

tion of a metal deactivator. Thus, the results of the 100° F. cabinet storage test particularly illustrate the effectiveness of the additives of the present invention as stabilizers for home heating oils.

Examination of the results of the high temperature tests shows that the additives of the present invention improve the stability of fuels under most of these conditions. It is preferred, however, when using the distillate fuels as diesel fuels, to incorporate in addition to the additives of the present invention minor amounts of a metal deactivator. As shown, the combination of a minor amount of metal deactivator with the additives of the present invention produces an excellent stabilizer for diesel fuels.

EXAMPLE II

A series of oxyalkylated products were prepared having the compositions shown in Table III.

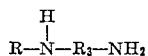
Table III

No.	Composition		Oxalkylated base—Composition					Oxalkylation temp., ° F.
	Percent oxyalkylated base	Percent xylene percent	Fatty diamine, percent	Ethylene oxide, percent	Propylene oxide, percent	Catalyst		
						Percent	Type	
SS-1102 A	62.5	37.5	90	10		.45	Na methylate	330-350
A	66.7	33.3	75	25		.385	do	330-350
C	71.5	28.5	60	40		.30	do	330-350
D	74.9	25.1	45	55		.235	do	330-350
E	81.8	18.2	30	70		.15	do	330-350
SS-1147 A	69.1	30.9	79.5	10.25	10.25	None		320-340
B	73.3	26.7	65	17.5	17.5	.65	Na methylate	230-340
C	78.0	22.0	50	25	25	.5	do	320-340
D	81.7	18.3	40	30	30	.4	do	320-340
SS-1305 A	67.0	33.0	75	25		.75	do	310-330
B	70.1	29.9	65	35		.65	do	310-330
C	73.5	26.5	55	45		.55	do	310-330
D	77.4	22.6	45	55		.45	do	310-330
E	79.3	20.7	40	60		.40	do	310-330
F	81.4	18.6	35	65		.35	do	310-330
G	83.5	16.5	30	70		.30	do	310-330
SS-1315 A	80.0	20.0	75	25		.21	do	300-320
B	83.4	16.6	60	40		.18	do	300-320
C	87.0	13.0	45	55		.14	do	300-320
D	91.0	9.0	30	70		.09	do	300-320
SS-1317 A	83.5	16.5	60	40		.15	do	300-320
SS-1319 A	80.0	20.0	75	25		None		300-320
B	83.5	16.5	60	40		.06	Na methylate	300-320
SS-1321 A	80.0	20.0	75	20	5	.375	do	300-320
B	83.5	16.5	60	32	8	.30	do	300-320
C	87.0	13.0	45	44	11	.225	do	300-320
D	91.0	9.0	30	56	14	.15	do	300-320

NOTE.—On series SS-1147 and SS-1321 ethylene and propylene oxides were mixed prior to injection into reactor.

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The fatty diamine in all instances was

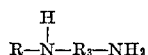


in which R_3 is trimethylene and R is a straight chain hydrocarbon residue derived from tallow acids containing 16-18 carbon atoms, while the alkylene oxide and the proportions reacted as well as the reaction temperatures and catalyst employed are shown in Table III.

Small amounts of the products thus prepared are added to the distillate fuel oil of Example I and tested as in Example I. All of the products show value as distillate fuel oil stabilizers.

We claim:

1. A fuel oil composition consisting essentially of a distillate fuel oil and a small amount sufficient to effectively stabilize said oil against deterioration of an oil-compatible reaction product of about 20 to 95 weight percent of a fatty diamine having the structural formula:



in which R is an aliphatic hydrocarbon chain of at least about 6 carbon atoms and R_3 is a divalent aliphatic hydrocarbon radical containing about 2 to 8 carbon atoms, and about 5 to 80 weight percent of an alkylene oxide of 2 to 4 carbon atoms.

2. The fuel oil composition of claim 1 in which the distillate fuel contains cracked components.

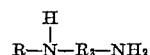
3. The fuel oil composition of claim 1 wherein the fatty diamine is about 30 to 70 weight percent and the alkylene oxide is about 30 to 70 weight percent.

4. The fuel oil composition of claim 1 wherein R_3 in the structural formula of the fatty diamine is trimethylene and R is the straight chain hydrocarbon residue derived from tallow fatty acids containing 16 to 18 carbon atoms and the alkylene oxide is ethylene oxide.

5. The fuel oil composition of claim 1 wherein the oxy-alkylated product is present in an amount ranging from about 5 pounds per 1000 barrels of fuel oil to 250 pounds per 1000 barrels of fuel oil.

6. The fuel oil composition of claim 4 wherein the oxy-alkylated product is present in amounts of about 5 pounds per 1000 barrels of fuel oil to 100 pounds per 1000 barrels of fuel oil.

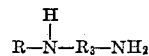
7. A fuel oil composition consisting essentially of a distillate diesel fuel and about 5 to 250 pounds per 1000 barrels of said fuel of an oil-compatible reaction product of about 20 to 95 weight percent of a fatty diamine having the structural formula:



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in which R is an aliphatic hydrocarbon chain of at least about 6 carbon atoms and R_3 is a divalent aliphatic hydrocarbon radical containing about 2 to 8 carbon atoms, and about 5 to 80 weight percent of an alkylene oxide of 2 to 4 carbon atoms, and about .25 to 2 pounds per 1000 barrels of said fuel of N,N'-disalicylidene-1,2-propylene diamine.

8. A fuel oil composition consisting essentially of a distillate diesel fuel and about 5 to 250 pounds per thousand barrels of said fuel of an oil-compatible reaction product of about 20 to 95 weight percent of a fatty diamine having a structural formula:



in which R_3 is trimethylene and R is a straight chain hydrocarbon residue derived from tallow fatty acids containing 16 to 18 carbon atoms, and about 5 to 80 weight percent of an alkylene oxide of 2 to 4 carbon atoms, and about .5 to 1 pound per thousand barrels of said fuel of N,N'-disalicylidene-1,2-propylenediamine.

9. The fuel oil composition of claim 1 in which the distillate fuel oil is a diesel fuel.

10. The fuel oil composition of claim 2 to which is added about .25 to 2 pounds per 1000 barrels of said fuel of N,N'-disalicylidene-1,2-propylene diamine.

11. The fuel oil composition of claim 1 wherein R is an aliphatic hydrocarbon chain of about 12 to 22 carbon atoms.

12. The fuel oil composition of claim 7 wherein R is an aliphatic hydrocarbon chain of 12 to 22 carbon atoms.

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