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(54) **Use of tertiary-alkyl primary amines in fuel compositions used as heat-transfer fluid**

Verwendung von tertiäralkylprimären Aminen in Brennstoffzusammensetzungen, die als Wärmeträgerfluid verwendet werden

Utilisation d' amines primaires avec un alkyle tertiaire dans des compositions de combustible utilisées en tant que fluide caloporteur

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(73) Proprietor: **ROHM AND HAAS COMPANY**
Philadelphia, Pennsylvania 19106-2399 (US)

(72) Inventors:
- **Banavali, Rajiv Manohar**
  Houston, Texas 77062 (US)
- **Chheda, Bharati Dinkar**
  Houston, Texas 77068 (US)

(74) Representative: **Kent, Venetia Katherine et al**
Rohm and Haas (UK) Ltd.,
European Patent Department,
28th Floor,
City Point,
One Ropemaker Street
London EC2Y 9HS (GB)

(56) References cited:
EP-A- 0 890 570
US-A- 2 456 569
US-A- 2 945 749
US-A- 3 014 793
US-A- 4 482 355

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Description

[0001] This invention relates to improved fuel oil compositions. Particularly, to fuel oil compositions containing cetane improvers having improved thermal stability The compositions further enjoy improved stabilization against: 1) sediment formation, and 2) color degradation during storage and distribution as well as improved cetane number, rust inhibition and demulsibility.

[0002] The useful life of a fuel is a function of its quality and of storage conditions. For instance, depending on the crude source and amount of cracked fraction, middle distillate fuels, such as diesel, jet fuels and heating fuels, can contain very different amounts of gum and color precursors, waxes, aromatics, and other products. Fuel storage stability was a well-understood problem prior to the introduction of low-sulfur diesel fuel. It is well established that diesel fuels can exhibit instability when stored for extended periods of time (storage stability), or when brought into contact with high temperature engine parts (thermal stability). Hydrotreating to meet 1993 regulations reduced storage stability problems for highway fuels. However, low-sulfur fuels resulted in other issues, such as peroxide and thermal stability problems in distillate fuels. However, fuels are often stored for much longer periods because of logistical and economic necessities.

[0003] The oxidative degradation products, formed under both prolonged storage and thermal stress, continue to be a problem in the utilization of, for example, diesel fuels. Fuel-instability reactions are defined in terms of the formation of deleterious products, such as filterable sediment, adherent gums, and peroxides. Sediments and gums which result from the oxidation reactions act to block filters and deposit on surfaces. Both the low-temperature storage and high-temperature thermal degradation, are of concern. Hydrotreating is generally considered the most effective means of improving stability. However, the cost of stability improvement by additives doping can often be less than the hydrotreatment costs.

[0004] The use of cetane improvers and the advent of more complicated diesel fuel utilization compounds problems of stability. Stringent diesel engine emissions regulations are being implemented worldwide. In the United States, the 1990 Clean Air Act mandated lowering NO_x emissions to 4.0 grams per horsepower-hour (g/hp-hr) for the 1998 model year. Future proposals by the U.S. Environmental Protection Agency (EPA) call for further reduction of combined NO_x and hydrocarbon emissions of heavy-duty trucks and buses to 2.5 g/hp-hr for the 2004 model year. Such reductions will require a combination of new engine technology and economically viable low-emission diesel fuels.

[0005] Numerous studies by the Coordinating Research Council and others have shown that increasing the cetane number by using additives significantly reduces carbon monoxide and NO_x emissions; hydrocarbon and particulate matter are slightly reduced. Cetane improvers also enhance the cold startability of diesel cars and trucks. Higher cetane can reduce white smoke, noise, misfire, emissions and improve cold starting in some engines. Diesel fuel with at least a 47 cetane number (measured by ASTM D 613) would qualify for the list.

[0006] Most users are knowledgeable about the fuel's primary role as an energy source. However, few are aware that diesel fuel performs multiple functions in a diesel engine and the associated fuel system. In addition to its primary role as an energy source, the fuel also serves as the sole lubricant of critical moving parts and as a heat-transfer fluid. Diesel fuel is increasingly used as a circulating coolant for high pressure fuel injections systems. This causes a problem in that as engine heat passes from injectors into the fuel, it can trigger a process that leads to particle formation, thus clogging filters and injectors. Fuels resistant to such thermal degradation must get a minimum 80% reflectance measurement using a green filter in the updated Octel F21-61 test (180 minutes, 150°C).

[0007] Adequate thermal stability is a necessary requirement for the effective functioning of diesel fuel as a heat-transfer fluid. In modern heavy-duty diesel engines, only a portion of the fuel that is circulated to the fuel injectors is actually delivered to the combustion cylinders. The remainder is circulated back to the fuel tank carrying heat with it, consequently raising the bulk fuel temperature. Because of the recirculation of fuel through the newer engines, fuel can be exposed momentarily to temperatures as high as 350°C. This process, in some engines and fuel combinations, could accelerate the instability of the diesel fuel. In some cases, this stress can cause the fuel to degrade and form insoluble materials that can restrict fuel flow through filters and injection systems.

[0008] Good thermal stability may become even more important in the future. Diesel engine manufacturers have indicated that engines under development to meet future exhaust emission standards will expose the fuel to more severe operating environments (stress), e.g., higher pressures and longer contact with high-temperature engine parts. In particular, thermal stability can be troublesome in some heavy-duty applications in some areas with widespread use of cetane improvers. Accordingly, cetane improvers will become increasingly important as engine makers promote and/or require higher cetane fuels, especially in premium diesel products.

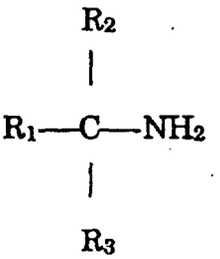
[0009] Additives can cause diesel fuel degradation if they are not oxidatively stable. Above 120°C, a cetane improver may oxidize and decompose, leading to particulate and sediment problems that can block filters. It is commonly accepted that 2-ethylhexyl nitrate functions as a diesel ignition improver because it is unstable, i.e., it thermally begins to decompose at about 155°C (311°F), i.e., just above the 300°F stability test temperature (Bacha, John; Lesnini, D. G., *Proceedings of the 6th International Conference on stability and Handling of Liquid Fuels,* 1997, Eds., H. N.; US

Dept. of Energy, Vol. 2, 671). This result suggests that the stability test temperature and test duration together are just sufficient for 2-ethylhexyl nitrate to contribute to the observed fuel thermal instability in the 300°F test.

[0010] Accordingly, there is a need for a fuel additive which imparts thermal stability to fuels even in the presence of cetane improver additives. Tertiary alkyl amines are known as diesel fuel additives as antioxidants for storage improvement (*see U.S. Patent 2,945,749*); in combination with fatty amines to counteract tendency of fatty amines to emulsify (see *U.S Patent 3,014,793*); to minimize coking, especially throttling nozzed coking, in the prechambers or swirl chambers of injection compression ignition engines US-A-4,482,355; and as stabilizers in combination with detergent, rust preventors and demulsifier additives (see *U.S. Patent 2*, *793*, *943*). However, none of these references discusses the use of tertiary alkyl primary amines as thermal stabilizers and cetane improvers especially in the presence of conventional cetane improvers.

[0011] The present inventors, have now unexpectedly found that fuels are made thermally stable in the presence of cetane improvers, which are known to make fuels thermally unstable, by the addition of tertiary alkyl primary amines in the C_8- C_{24} range . Furthermore, the tertiary alkyl primary amines of the present invention also operate as cetane number improvers and the combination of cetane number improvers with the tertiary alkyl primary amines of the present invention provide a higher cetane number than that provided by the cetane improver alone. Also, fuel oil compositions containing these amines are also characterized as having improved dispersability, improved rust inhibition and improved demulsibility.

[0012] In a first aspect of the present invention, there is provided the use in a fuel composition which is used as a heat-transfer fluid in a heavy duty diesel engine, said composition comprising: (A) a major amount of diesel fuel; (B) at least one cetane number improver; of from 1 to 1000 ppm of at least one tertiary (C_8-C_{24}) alkyl primary amine of the formula:



wherein: R_1, R_2, and R_3 are each independently (C_1-C_{21}) alkyl, substituted (C_1-C_{21}) alkyl, (C_1-C_{21}) alkenyl or substituted (C_1-C_{21}) alkenyl.

[0013] As used herein the terminology "(C_1-C_{21})" means a straight chain or branched chain alkyl group having from 1 to 21 carbon atoms per group.

[0014] Also, the term "major amount" is understood to mean greater than 50 percent by weight and the term "minor amount" is understood to mean less than 50 percent by weight.

[0015] Throughout this specification and claims, unless otherwise indicated, references to percentages are by weight, all temperatures by degree centigrade and all pressures are atmospheric.

[0016] It is also to be understood that for purposes of this specification and claims that the range and ratio limits, recited herein, are combinable. For example, if ranges of 1-20 and 5-15 are recited for a particular parameter, it is understood that ranges of 1-15 or 5-20 are also contemplated.

[0017] Generally, the diesel fuel is present in a major amount in the fuel composition. In a preferred embodiment, the diesel fuel is present in an amount of at least 60% by weight, preferably at least 75% by weight, more preferably at least 90% by weight of the total fuel composition.

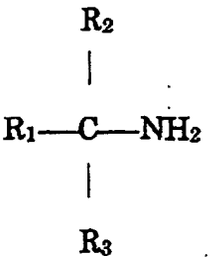
[0018] The fuel compositions also include at least one cetane improver. Cetane improvers are compounds that readily decompose to form free radicals and then, in turn, promote the rate of chain initiation. The increased rate of chain initiation improves ignition characteristics for diesel fuel. Accordingly, cetane number (ignition quality) improvers are used to increase the cetane number when the base fuel cetane does not meet required specifications. Suitable cetane improvers include, without limitation, alkyl nitrates, such as 2-ethylhexyl nitrate (2-EHN); peroxides, such as di-t-butylperoxide; tetrazoles; thioaldehydes, tertiary alkyl primary amines, and mixtures thereof. In a preferred embodiment, the at least one cetane improver is an alkyl nitrate. In a more preferred embodiment, the at least one cetane improver is 2-ethylhexyl nitrate (2-EHN).

[0019] In one embodiment, the at least one cetane improver is a tertiary alkyl primary amine. In a preferred embodiment, the at least one cetane improver is a tertiary alkyl primary amine and the fuel composition further includes a

second cetane improver selected from alkyl nitrates, peroxides, tetrazoles; thioaldehydes, tertiary alkyl primary amines, and mixtures thereof. In a more preferred embodiment, the at least one cetane improver is a tertiary alkyl primary amine and the fuel composition further includes a second cetane improver which is an alkyl nitrate, such as 2-EHN.

[0020] Generally, the cetane improver is present in the fuel composition at a concentration of 50 to 7500, preferably 100 to 5000, more preferably 100 to 2000 ppm.

[0021] The at least one tertiary alkyl primary amine is a tertiary (C_8-C_{24}) alkyl primary amine according to the formula:



wherein: R_1, R_2, and R_3 are each independently (C_1-C_{21}) alkyl, substituted (C_1-C_{21}) alkyl, (C_1-C_{21}) alkenyl or substituted (C_1-C_{21}) alkenyl.

[0022] Suitable examples of (C_1-C_{21}) alkyl include, but are not limited to, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, isopentyl, neopentyl, n-hexyl, 2-ethylhexyl, octyl, decyl, isodecyl, undecyl, dodecyl (also known as lauryl), tridecyl, tetradecyl (also known as myristyl), pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, cosyl, and eicosyl.

[0023] Suitable examples of (C_1-C_{21}) alkenyl include, but are not limited to, ethenyl, n-propenyl, isopropenyl, 1-butenyl, cis-2-butenyl, isobutylene, trans-2-butenyl, 2-3, dimethyl-2-butenyl, 3-methyl-1-butenyl, 2-methyl-2-butene, 1-pentenyl, cis-2-pentenyl, trans-2-pentenyl, 1-hexenyl, 1-heptenyl, 1-octentl, 1-nonenyl, and 1-decenyl.

[0024] Suitable examples of (C_1-C_{21}) substituted alkyl and alkenyl include, but are not limited to, the above recited alkyl and alkenyl groups substituted with hydroxy, halide such as fluorine, chlorine or bromine; cyano; alkoxy; haloalkyl; carbalkoxy; carboxy; amino; alkylamino derivatives and the like; or nitro groups.

[0025] The at least one tertiary alkyl primary amine may be a single amine or a mixture of amines, for instance as described following. In one embodiment, the at least one tertiary alkyl amine is 1,1,3,3-tetramethylbutylamine available from Rohm and Haas Co of Philadelphia, PA as PRIMENE TOA®. In another embodiment, the at least one tertiary alkyl amine is an isomeric mixture of C_{16} to C_{22} tertiary alkyl primary amines available from Rohm and Haas Co of Philadelphia, PA as PRIMENE JM-T®. In a preferred embodiment, the at least one tertiary alkyl amine is an isomeric mixture of C_8 to C_{10} tertiary alkyl primary amines available from Rohm and Haas Co of Philadelphia, PA as PRIMENE BC-9® or an isomeric mixture of C_{12} to C_{14} tertiary alkyl primary amines available from Rohm and Haas Co of Philadelphia, PA as PRIMENE 81-R® or a mixture of PRIMENE BC-9® and PRIMENE 81-R®. In a more preferred embodiment, the at least one tertiary alkyl amine is an isomeric mixture of C_{12} to C_{14} tertiary alkyl primary amines available from Rohm and Haas Co of Philadelphia, PA as PRIMENE 81-R®.

[0026] Generally, the at least one tertiary alkyl primary amine is present in the fuel composition at a concentration of 1 to 1000, preferably 5 to 500, more preferably 10 to 200 ppm, most preferably 10 to 100 ppm. In another embodiment, the at least one tertiary alkyl primary amine is present in the fuel composition at a concentration of 50 to 100, or 1 to 10 ppm.

[0027] The tertiary alkyl primary amines used in the fuel compositions are prepared using substrate compounds known as substrates for the Ritter reaction and include, for example, alcohols, alkenes, aldehydes, ketones, and ethers, (*see, generally, L. I. Krimen and D. J. Cota, "The Ritter Reaction", Organic Reactions, Vol. 17, 1969, pp. 213-325).* Processes for preparing tertiary alkyl primary amines are known in the art and are described for instance in U.S Patent 5,527,949 and in co-pending provisional application 60/051,867.

[0028] The fuel compositions may also include other additives well known in the art such as, without limitation, antioxidants, dispersants, anti-foaming agents and the like.

[0029] The following Examples are provided as an illustration of the present invention. Fuel samples #A- # I were fresh test fuels without any additives and were obtained from commercial sources. The fuel samples were analyzed to ensure conformance with specifications and stored under ambient temperature, in dark, and under nitrogen atmosphere. All of the C_8, C_9, C_{12}, and C_{18} tertiary alkyl primary amines samples were commercial products sold under the trademark Primene® by Rohm and Haas Company of Philadelphia, Pa. The results are shown in Table 1.

Table 1

Detailed Analysis of Test Fuel Samples									
Test	**Fuel # A**	**Fuel # B**	**Fuel # C**	**Fuel # D**	**Fuel # E**	**Fuel # F**	**Fuel # G**	**Fuel # H**	**Fuel # I**
Sulfur vol%	0.241	0.4	0.047	0.035	0.038	0.04	1.8	0.1974	0..224
Aromatics vol %		27.5	25	28.1	27.8	27.9			25.5
Olefins vol %		1.7	1.3	1.9	1.8				2.1
Saturates vol %		70.8	73.7	70	70.4				72.4
Cetane Number	49.9	51.5	47		45.4	47	34	40.3	38

Example 1

[0030] Fuel #A was evaluated for thermal stability and cetane number improvement. A sample of Fuel #A containing 100 ppm Primene® 81-R and a sample without were prepared. The fuel samples were stored in an air atmosphere at room temperature during the test period.

[0031] The fuel samples were tested for a prolonged period of storage stability. Periodically, as indicated in Table 2, the fuels were sampled and tested for oxidative stability according to ASTM D 2274 Diesel Oxidation Stability test method as follows. A 350 mL sample of fuel was heated at 95°C for 40 hr. while oxygen is bubbled through at the rate of 3 liters per hour. After aging, the sample is cooled to room temperature and filtered to obtain the filterable insoluble quantity. Adherent insolubles are then removed from the associated glassware with trisolvent (TAM). The TAM is then evaporated to obtain the adherent insolubles. The sum of filterable and adherent insolubles, expressed as milligrams per 100 mL, is reported as total insolubles. A total sediment of 1 mg/100 mL or less is generally acceptable to pass the test, anything above 1 mg/100 mL sediment results in failing the test. The results are shown in Table 2 following.

Table 2.

Comparison of the Results from Oxidation Stability of diesel Fuel #A @ No. of Weeks by ASTM D 2274		
No. of Weeks of Storage	**Total Sediments (mg/100ml)**	
	Diesel Fuel #A	**Diesel Fuel #A + 100 ppm Primene® 81-R**
2	1.0	0.2
5	2.2	0.5
7	2.8	0.6
10	19	1.0
15	27	2.2

The highest sediment reported in the Table 2 is 27mg for diesel Fuel #A, which is an indication of instability of the fuel at the prolonged period of time. The test results shown in Table 1 exhibit the better stability for fuel #A with 100 ppm 81-R added , at the extended period of time. It is evident that Primene® 81-R is acting as a stabilizer in the diesel fuel, by helping to prevent gum/sediment formation. The most noteworthy point from these results is that Fuel #A containing 100 ppm of Primene® 81-R showed that the fuel is stable even after 10 weeks compared to Fuel #A without Primene® 81-R.

[0032] The Fuel #A samples were also tested for cetane number with and without additives. The method used for cetane number determination was ASTM D 613 as well as tested for oxidation stability using ASTM D 2274. The results are shown in Table 3.

Table 3. Oxidation Stability Test Results by ASTM D 2274 and Cetane # by ASTM D 613 for Fuel #A

ppm Additives	Total Insolubles, mg/100mL		Cetane Number	
	Diesel #A	Diesel #A + 100 ppm Primene® 81-R	Diesel #A	Diesel #A + 100 ppm Primene ® 81-R
None(@ 0 weeks)	1	0.3	49.9	50.6
100 ppm Primene® 81-R	0.2	0.2		
1000 ppm 2-EHN#	2.1	---	53.1	
1000 ppm 2-EHN + 100 ppm Primene® 81-R	0.1		53.4	
1000 ppm 2-EHN + 100 ppm Primene® 70/30*	0.1	< 0.1	53.7	
none (@ 5weeks.)	2.2	0.5	51.0	51.5
100 ppm Primene® 81-R	0.3			
100 ppm Primene® 70/30*	0.7			
None (@ 7 weeks.)	2.8	0.6		
None (@ 10 weeks.)	19	1.0		
None (@ 15 weeks.)	27	2.2		

*Primene 70/30 = Blend of 70% Primene 81-R and 30% Plexol® 917T

#2-EHN = 2-ethylhexylnitrate

Addition of 2-ethylhexylnitrate (2-EHN) improves the cetane number, but lowers the oxidative storage stability of the fuel #A as seen in Table 3. Addition of 100 ppm of Primene® 81-R to the fuel #A with 1000 ppm 2-EHN increases the storage stability without sacrificing the effect of 2-EHN as seen in the results in Table 3. Thus Primene® 81-R is not only a stabilizer additive for the diesel fuel by itself, but, also is thermal stabilizer and synergistic cetane improver. Additionally, the tertiary alkyl primary amine (Primene®) enhances the cetane number both with and without the presence of conventional cetane improvers.

Example 2

[0033] A sample of diesel fuel #B obtained from a Texas Gulf Coast Area refinery was tested for oxidation stability using Primene amines and other primary amines using the ASTM D 2274 test method for 40 hr. The results given in Table 4 show that the Primene 81-R and Primene BC-9 are acting as stabilizers, and help in improving the oxidative storage stability. Other primary amines did not exhibit properties as stabilizers.

Table 4. Oxidation Stability Results for Diesel Fuels #B (ASTM D 2274 @ 40 hr.)

Additives	Dosage	Fuel #B
		mg/100mL
None	—	2.3
Primene® 81-R	100	<0.1
Primene® JM-T	100	0.1
Primene® TOA	15	0.4
Primene® BC-9	15	<0.1
Primene® 81-R	15	1.2
Primene® JM-T	15	1.4
TAPA C-13-16 blend	15	<0.1
TA PA C16-18 blend	15	1.9
isononylamine	15	2.1
n-nonylamine	15	1.9
2-ethylhexylamine	15	2.2
n-dodecylamine	15	2.2
n-Octadecylamine	15	2.4

Example 3

[0034] Samples of fuel #C, #D, and #E having a sulfur concentration of 0.047%, 0.035%, and 0.035%, respectively were also evaluated for thermal stability and cetane number improvement. The cetane numbers of these fuels are listed in Table 5, and found to be 44.1, 45.5, and 45.4 respectively for the fuel # C, #D, and #E. The fuels were tested for oxidation/thermal stability with and without 2-EHN and combined with Primene amines. 2-EHN is used as a cetane number improver additive, and the addition of 2-EHN does increase the cetane number. However, it has an adverse effect on the thermal stability of the fuel when subjected to the Octel/DuPont F21-61 test at 150°C for 90 minutes. The Octel/DuPont F21-61 test was done as follows. A 50 mL sample of fuel oil in a test tube is stored in a 300°F bath for 90 minutes (or 180 Min.). After removal from the bath it is allowed to cool to room temperature (about 2 hr.). The aged fuel is then filtered through 4.25 cm Whatman No 1 filter paper. The paper is then washed with heptane and the color of the filter paper is compared to a set of standards (1 = No color, 20 = dark brown).

[0035] Addition of 100 ppm of Primene 81-R helped in increasing the thermal stability while also increasing the cetane number in the presence of 2-EHN as seen in the results in Table 5.

[0036] The Octel/DuPont F21-61 test also evaluates the filter pad by comparing with a standard filter color chart provided by Octel/DuPont. A rating of up to 7 is generally considered as a pass, and anything above 7 is considered a fail. The data presented in the Table 5 show that the addition of 2-EHN in all three fuel samples increased the filter pad rating to failure, 16, 10, and 9 for the fuels # C, #D, and #E respectively. Furthermore, the addition of Primene 81-R in the presence of 2-EHN increased the thermal stability in terms of pad rating and color and increased the cetane number as well.

Table 5.

Octel/Du Pont F21-61 @ 90 min. & Cetane Number Test Results of Diesel fuel # C, #D, & #E									
	Diesel Fuel #C			Diesel Fuel #D			Diesel Fuel # E		
Additive(ppm)	Cetane No.	Thermal Stability Using DuPont F-21 Test Method, (filter pad rating)		Cetane No.	Thermal Stability Using DuPont F-21 Test Method		Cetane No.	Thermal Stability Using DuPont F-21 Test Method	
		color before/ after	Filter pad rating		color before/ after	Filter pad rating		Color before/ after	Filter pad rating
None	44.1	1.0/1.5,	2	45.5	1.0/1.0	2	45.4	1.5/2.5	3
70% Primene®81-R / 30% Plexol®917T (100)	44.4	1.0/1.0	1	45.9	1.0/1.0	1	45.4	1.5/2.5	2
2-EHN (1000)	48.1	1.0/3.0	16	48.5	1.0/3.0	10	48.3	1.5/3.5	9
2-EHN (1000) +Primene® 81-R/Plexol®917T (100)	47.6	1.5/1.5	1	50	1/2	1	48.4	1.5/3	1
2-EHN (1000) + Primene®81-R (70)	47.8	1.0/1.5	1	48.7	1.0/1.5	1	48.8	1.5/3.0	1

Example 4

[0037] The fuel was subjected to Octel/DuPont F21-61 test for 180 minutes. The results showed that 2,6-di-t-butyl-4-methyl phenol and N,N'-di-sec-butyl-p-phenylenediamine are not effective anti-oxidants at 20 or 40 ppm concentration under these test conditions. The results shown in Table 6 also suggest that the Primene amines, and dinonyl diphenylamine are effective thermal stabilizers at 40 ppm concentration under these test conditions. However, the combination of Primene 81-R and Primene BC-9 at 1:1 ratio is effective, at 20 ppm concentration, to increase the thermal stability of the test fuel.

Table 6. Thermal Stability Test Results of Fuel #F (Octel/Du Pont F21-61 @ 180 min.)

Additives		Octel/Du Pont F 21-61 Stability test @ 180 min.	
	(ppm)	Color, before/after	Filter pad rating
None		1.5/2.0	13
Primene® 81-R	20	1.0/2.0	9
Primene®BC-9	20	0.5/1.5	10
Primene® 81-R + Plexol® 917T*	20	0.5/2.0	7
2,6-di-t-butyl-4-methyl phenol	20	0.5/1.5	11
N,N'-di-sec-butyl-p-phenylenediamine	20	0.5/2.5	14
Dinonyl diphenylamine	20	1.0/2.0	9
Primene® JM-T	20	1.0/2.0	8
Primene® 81-R+ Primene® BC-9 (1:1)	20	1.0/2.0	3
Dinonyl diphenylamine	40	3.0/3.0	3
N.N'-di-sec-butyl-p-phenylenediamine	40	0.5/2.5	14
2,6-di-t-butyl-4-methyl phenol	40	0.5/2.0	12
Primene® 81-R	40	1 / 1.5	1
Primene® BC-9	40	1 / 1.5	1

* a blend of 70% Primene® 81-R + 30% Plexol® 917T

Example 5

[0038] Testing of fuel # F was extended to evaluate the effect of 2-EHN in the presence and absence of stabilizers. It was learned from Example 3 that the addition of 2-EHN lowers the thermal stability, however the test was run for 90 minutes in Example 3. For fuel #F the cetane number tests showed an increase in cetane number by an average of 7 units with the addition of 2000 ppm of 2-EHN. It was also observed that the addition of 2-EHN decreases the thermal stability, which is reclaimed by the addition of Primene® amines at 100 ppm level. The focus of this experiment was to determine the effect of stabilizers in the presence of 2-EHN, and a comparison was made using Primene® amines and dinonyl diphenylamine only. The results shown in Table 7 suggest that dinonyl diphenylamine failed to stabilize fuel in the presence of 2-EHN. The addition of Primene® amines showed progressively increased thermal stability as the concentration increased. The increased addition of Primene® amine concentration showed a decrease in filter pad rating.

Table 7 Test Results of Thermal Stability and Cetane Number Improver for Fuel #F

Additives (ppm)	Octel/DuPont F21-61 Test @ 180 Minutes		Cetane Number
	Color, before/after	Filter pad Rating	
None	1.5 /2.5	13	47
2-EHN (2000)	1 / 7.5	14	54.3
2-EHN (2000) + Primene® 81-R (20)	1 / 7	13	54.3
2-EHN + Dinonyl diphenylamine (20)	1 / 7.5	15	53.4
2-EHN (2000) + Primene® 81-R (40)	1 / 6	13	55.2
2-EHN (2000) + Dinonyl diphenylamine (40)	1 / 7.5	16	54.3
2-EHN (2000) + Primene® BC-9 (40)	1 / 6.5	13	54.3
2-EHN (2000) + Primene® 81-R + Primene® BC-9 (1:1) (40)	1 / 6	10	54.9

[0039] The results shown in Table 8 were from continued testing of diesel Fuel #F to improve thermal stability in the presence of 2-EHN. The results showed that Primene® 81-R, and Primene® BC-9 and a combination of both at 100 ppm concentration with 2000 ppm of 2-EHN is effective in improving the thermal stability of the fuel. The combination of 2-ethylhexylnitrate and Primenes® improves the cetane number of the base fuel more than 2-EHN alone. Table 7 represents the relationship between the concentration of the additives, cetane number, and the filter pad rating of the DuPont F-21 test.

Table 7 Test Results of Thermal Stability and Cetane Number Improver for Fuel #F

Additives (ppm)	Octel/DuPont F21-61 Test @ 180 Minutes	
	Color, before/after	Filter pad Rating
2-EHN (2000) + Primene® 81-R (80)	1 / 5.5	8
2-EHN (2000) + Primene® 81-R + Primene® BC-9 (1:1) 80 ppm	1 / 5.5	8
2-EHN (2000) + Dinonyl diphenylamine (80)	1 / 8.0	16
2-EHN (2000) + Primene® 81-R (100)	1 / 4	6
2-EHN (2000) + Primene® BC-9 + Primene® 81-R, 1:1 (100)	1 / 4	6
2-EHN (2000) + Primene® BC-9 (100)	1 / 4	6
2-EHN (2000) + Dinonyl diphenylamine (100)	1 / 7	16

Example 6

[0040] Fuel oil samples of 500 mL were stored in 600 mL beakers covered with watch glasses in oven at 40°C. At

arbitrary intervals, optical density measurements were made on samples before and after filtering a small portion of vigorously shaken sample through a CORNING 30 F fritted glass crucible. The unused portion was immediately returned to the oven for further aging. The failure time was determined by three methods: 1) the number of days to a stated level of optical density difference (Δ OD) of 0.12 between unfiltered portions, 2) days to reach an OD value of 1.00 for the unfiltered sample, and 3) days to reach a residue level of 2.0 mg/100 mL as determined by filtration. The results shown in Table 9 shows that addition of Primene® 81-R prolonged the decomposition period for the diesel by detecting the OD = 1 after 120 days compared to the commercially used antioxidants, hence increasing the storage stability with respect to both color and sediment.

Table 9 Long Term Storage Stability Test Results for Fuel Oil # G

Additive	Dosage (ppm)	Days to failure by		
		Δ OD = 0.12	OD = 1.0	2 mg/100 mL
None	----	35	70	59
Primene® 81-R	30	95	120	76
Commercial AO #21	30	40	88	58
Commercial AO #2	30	65	108	75

Example 7

[0041] Thermal stability tests were determined for Fuel # H and # I which are diesel fuels made from blending straight-run distillates with Light cycle Oil(LCO). Once again, the results given in Table 10 show that Primene® amines improve the thermal stability.

Table10. Octel/DuPont F21-61 @ 180 min. Thermal Stability Test (No. 2-D Diesel)

Additive	Dosage (ppm)	Refinery Sample* # H		Refinery Sample* # I	
		Filter Pad Rating	ASTM Color	Filter Pad Rating	ASTM Color
None	---	11	2.5	16	6
Primene® 81-R	7.5	3	2	3	4
Primene® 81-R	15	2	2	4	3.5
Commercial AO #1	7.5	5	2	6	4
Commercial AO #1	15	2	2	4	4
Commercial AO #2	7.5	3	2	10	3.5
Primene® 81-R +MDA	7.5+1.5	3	2	4	4
Primene® 81-R +Dispersant	7.5+7.5	3	2	3	4
Primene® 81-R +Dispersant ♦ +MDA ❖	7.5+7.5+1.5	7	2	7	3.5

❖MDA metal deactivator - N,N'-Disalicylidene-1,2-propylenediamine

♦ Dispersant - Plexol® 917T

*The samples contained a blend of straight-run distillate and light cycle oil(LCO)

Example 8

[0042] Presence of water or any other additives reacting water could form an emulsion in the fuel. ASTM test method D-1094 is utilized to test the water reaction of the fuels. Primene® amines show the capability of enhancing the fuel demulsibility property. Table 10 show the results of ASTM D 1094 demonstrating the ability of Primene amines to extract

water soluble compounds and keep them soluble in fuel layer.

Table 10

Test Results of ASTM D 1094				
Additive	**Separation Rating**	**Interface Appearance Rating**	**Free Water separation (mL)**	**Appearance of Fuel layer**
Blank	2 (small air bubbles in the fuel layer)	2 (2mL of lace)	19 (clear)	slightly hazy
9.7 ppm Primene® JM-T	2 (small air bubbles in the fuel layer)	2 (1mL of lace)	18 (oil bubbles in water layer)	hazy
9.7 ppm Plexol® 917 T	3 (fuel layer - emulsion)	1b (loose lace at the interface)	20	Fuel layer - cloudy, emulsion
9.7 ppm Primene® JM-T + 9.7 ppm Plexol® 917 T	2 (small air bubbles in the fuel layer)	1b (loose lace at the interface)	20	slight hazy (like blank)
9.7 ppm Triton® CF-32*	2	1	20	hazy -Like blank

*surfactant available from Union Carbide, Danbury, Ct.

[0043] The results of the various stability tests as measured by color, sediments and gum formation show (See above) clearly shows that the addition of tertiary alkyl primary amines, at a few ppm levels, significantly improves the stability of fuel oils and diesel. It also shows that the stability of diesel containing a catalytically cracked fraction blend can be improved by Primene® 81-R doping at 30 ppm. Several commercial fuel stabilizers at the same dosage level show similar or worse performance.

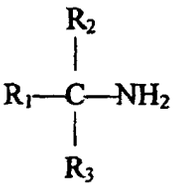
[0044] Oxidative and thermal stability of diesel fuels was studied on fuel samples (a) collected from major regions around the world; (b) containing both high and low levels of sulfur and (c) containing both straight run and cracked components. The results of the various stability tests as measured by color, sediments and gum formation show clearly that addition of tertiary alkyl primary amines, at few ppm levels, significantly improves the stability of fuels. Results show that the thermal stability of both low and high sulfur fuels can be improved by tertiary alkyl primary amines doping at 8-40 ppm range. Furthermore, thermal stability is achieved without negatively effecting the cetane number. In fact, the cetane number is improved.

[0045] It is noteworthy that both sedimentation and color are improved by tertiary alkyl primary amines. The results of oxidative stability of diesel showing similar tertiary alkyl primary amines benefits were shown earlier. Several commercial fuel stabilizers at the same dosage level show similar or worse performance. The data that tertiary alkyl primary amines are equal or better stabilizers is also seen in comparative experiments with several well-known common fuel stabilizers.

Claims

1. Use in a fuel composition that is used as a heat-transfer fluid in a heavy duty diesel engine, said composition comprising:

(A) a major amount of diesel fuel, and
(B) a minor amount of at least one cetane number improver, of from 1 to 1000 ppm of at least one at least one tertiary (C_8-C_{24})alkyl primary amine of the formula:



wherein the R_1, R_2, and R_3 are each independently (C_1-C_{21}) alkyl, substituted (C_1-C_{21}) alkyl, (C_1-C_{21}) alkenyl or substituted (C_1-C_{21}) alkenyl, to improve the thermal stability of said composition.

2. The use of claim 1, wherein the at least one cetane improver is present at a concentration 50 to 7500 ppm.

3. The use of claim 1, wherein the at least one cetane improver is 2-ethylhexylnitrate.

4. The use of claim 1, wherein the at least one tertiary alkyl primary amine is a C_9 tertiary alkyl amine.

5. The use of claim 1, wherein the at least one tertiary alkyl primary amine is a C_{12} tertiary alkyl primary amine.

6. The use of claim 1, wherein the at least one tertiary alkyl primary amine is a C_{18} tertiary alkyl primary amine.

7. The use of claim 4, wherein the fuel composition further comprises a C_{12} tertiary alkyl primary amine.

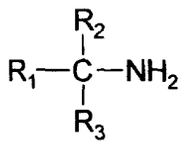
8. The use of claim 1, wherein the at least one cetane improver is a tertiary alkyl primary amine.

9. The use of claim 8, further comprising a second cetane improver selected from alkyl nitrates, peroxides, tetrazoles, thioaldehydes, tertiary alkyl primary amines, and mixtures thereof.

Patentansprüche

1. Verwendung einer Treibstoffzusammensetzung die als Wärmeübertragungsflüssigkeit in einem Hochleistungsdieselmotor verwendet wird, wobei die Zusammensetzung umfasst:

(A) eine Hauptmenge an Dieseltreibstoff, und
(B) eine Nebenmenge mindestens einen Cetanzahlenverbesserers, und 1 bis 1000 ppm mindestens eines primären (C_8 bis C_{24}) Alkylamins der Formel:



worin R_1, R_2 und R_3 unabhängig voneinander (C_1-C_4) Alkyl, substituiertes (C_1-C_{21})Alkyl, (C_1-C_{21})Alkenyl oder substituiertes (C_1-C_{21})Alkenyl sind, um die thermische Stabilität der Zusammensetzung zu verbessern.

2. Verwendung nach Anspruch 1, wobei der mindestens eine Cetanverbesserer in einer Konzentration von 50 bis 7500 ppm vorliegt.

3. Verwendung nach Anspruch 1, wobei der mindestens eine Cetanverbesserer 2-Ethylhexylnitrat ist.

4. Verwendung nach Anspruch 1, wobei das mindestens eine primäre Tertiäralkylamin ein C_9-Tertiäralkylamin ist.

5. Verwendung nach Anspruch 1, wobei das mindestens eine primäre Tertiäralkylamin ein primäres C_{12}-Tertiäralky-

lamin ist.

6. Verwendung nach Anspruch 1, wobei das mindestens eine primäre Tertiäralkylamin ein primäres C_{18}-Tertiäralkylamin ist.

7. Verwendung nach Anspruch 4, wobei die Treibstoffzusammensetzung ferner ein primäres C_{12}-Tertiäralkylamin umfasst.

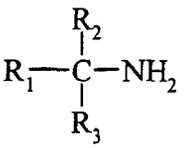
8. Verwendung nach Anspruch 1, wobei der mindestens eine Cetanverbesserer ein primäres Tertiäralkylamin ist.

9. Verwendung nach Anspruch 8, ferner umfassend einen zweiten Cetanverbesserer ausgewählt aus Alkylnitraten, Peroxiden, Tetrazolen, Thioaldehyden, primären Tertiäralkylaminen, sowie Mischungen davon.

Revendications

1. Utilisation, dans une composition de combustible qui est utilisée en tant que fluide caloporteur dans un moteur diesel à grande puissance, ladite composition comprenant :

   (A) une quantité principale d'un combustible diesel, et
   (B) une quantité secondaire d'au moins un agent améliorant l'indice de cétane, constituée de 1 à 1 000 ppm d'au moins une amine primaire à groupe alkyle tertiaire en C_8-C_{24} de formule



   dans laquelle R_1, R_2 et R_3 représentent chacun indépendamment des autres un groupe alkyle en C_1-C_{21}, alkyle en C_1-C_{21} substitué, alcényle en C_1-C_{21} ou alcényle en C_1-C_{21} substitué, pour améliorer la stabilité thermique de ladite composition.

2. Utilisation selon la revendication 1, pour laquelle l'au moins un agent améliorant l'indice de cétane est présent à une concentration de 50 à 7 500 ppm.

3. Utilisation selon la revendication 1, pour laquelle l'au moins un agent améliorant l'indice de cétane est le nitrate de 2-éthylhexyle.

4. Utilisation selon la revendication 1, pour laquelle l'au moins une amine primaire à groupe alkyle tertiaire est une tert-alkylamine en C_9.

5. Utilisation selon la revendication 1, pour laquelle l'au moins une amine primaire à groupe alkyle tertiaire est une tert-alkylamine primaire en C_{12}.

6. Utilisation selon la revendication 1, pour laquelle l'au moins une amine primaire à groupe alkyle tertiaire est une tert-alkylamine primaire en C_{18}.

7. Utilisation selon la revendication 4, pour laquelle la composition de combustible comprend en outre une tert-alkylamine primaire en C_{12}.

8. Utilisation selon la revendication 1, pour laquelle l'au moins un agent améliorant l'indice de cétane est une tert-alkylamine primaire.

9. Utilisation selon la revendication 8, qui comprend en outre un deuxième agent améliorant l'indice de cétane, choisi parmi les nitrates d'alkyle, les peroxydes, les tétrazoles, les thioaldéhydes, les tert-alkylamines primaires et leurs mélanges.