



EUROPEAN PATENT APPLICATION

Application number : **92309066.6**

Int. Cl.⁵ : **C10L 1/14, C10L 10/02**

Date of filing : **05.10.92**

Priority : **08.10.91 US 772933**

Date of publication of application :
21.04.93 Bulletin 93/16

Designated Contracting States :
BE DE ES FR GB IT

Applicant : **ETHYL PETROLEUM ADDITIVES,
INC.
20 South Fourth Street
St. Louis Missouri 63102-1886 (US)**

Inventor : **Cunningham, Lawrence Joseph
1928 Windyhill
Kirkwood, Missouri 63122 (US)**
Inventor : **Kulinowski, Alexander Michael
3840B Provence Drive
St. Louis, Missouri 63125 (US)**
Inventor : **Henly, Timothy James
7748 Ravensridge Road
St. Louis, Missouri 63119 (US)**

Representative : **Collier, Jeremy Austin Grey
J.A.Kemp & Co., 14 South Square, Gray's Inn
London WC1R 5LX (GB)**

Fuel compositions.

Fuels, methods of producing fuels, and methods of using fuels to reduce the amount of atmospheric pollutants (NO_x, CO, and/or hydrocarbons) formed on combustion of middle distillate fuels in engines or burner apparatus. These results can be achieved without an undesirable increase in emissions of particulates. The fuels contain less than 500 ppm of sulfur and at least one organic nitrate combustion improver and at least one tertiary alkyl peroxy ester alkanolate or peroxy benzoate.

This invention relates to preservation of the environment. More particularly, this invention relates to fuel compositions and methods that reduce atmospheric pollution normally caused by the operation of engines or combustion apparatus on middle distillate fuels.

5 The importance and desirability of reducing the release of pollutants into the atmosphere are well recognized. Among the pollutants sought to be reduced are nitrogen oxides ("NO_x"), carbon monoxide, unburned hydrocarbons, and particulates.

This invention involves the discovery, inter alia, that it is possible to reduce the amount of NO_x or CO or unburned hydrocarbons released into the atmosphere during operation of engines or other combustion apparatus operated on a fuel composition characterized in that it comprises a major proportion of a hydrocarbonaceous middle distillate fuel which has a sulfur content of less than 500 ppm and in that said fuel contains a minor emission reducing amount of (i) at least one organic nitrate combustion improver, and (ii) at least one tertiary alkyl peroxy alkanoate or peroxy benzoate dissolved therein. In fact it has been found possible through use of such fuel compositions to reduce the amount of two and in some cases all three such pollutants (NO_x, CO and unburned hydrocarbons) emitted by diesel engines. Moreover this important and highly desirable objective has been and thus may be achieved without suffering an undesirable increase in the emission of particulates. this is a unique discovery since the available experimental evidence and mechanistic theories of combustion suggest that if NO_x is reduced, the amount of particulates will be increased, and vice versa.

15 Accordingly this invention provides in one of its embodiments a fuel composition characterized in that it comprises a major proportion of a hydrocarbonaceous middle distillate fuel which has a sulfur content of less than 500 ppm (preferably 100 ppm or less and most preferably no more than 60 ppm) and in that said fuel contains a minor emission reducing amount of (i) at least one organic nitrate combustion improver and (ii) at least one tertiary alkyl peroxy alkanoate or peroxy benzoate of the formula



30 dissolved therein wherein R is a tertiary alkyl group of 4 to 8 carbon atoms and R' is a hydrocarbon group having 1 to 24 carbon atoms.

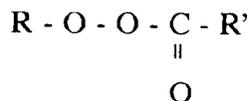
By the term "hydrocarbonaceous" as used in the ensuing description and appended claims is meant the middle distillate fuel is composed principally or entirely of fuels derived from petroleum by any of the usual processing operations. The finished fuels may contain, in addition, minor amounts of non-hydrocarbonaceous fuels or blending components such as alcohols, or like materials, and/or minor amounts of suitably desulfurized auxiliary liquid fuels of appropriate boiling ranges (i.e., between 160° and 370°C) derived from tar sands, shale oil or coal. When using blends composed of such desulfurized auxiliary liquid fuels and hydrocarbonaceous middle distillate fuels, the sulfur content of the total blend must be kept below 500 ppm.

In another of its embodiments this invention provides improvements in combustion processes wherein a hydrocarbonaceous middle distillate fuel is subjected to combustion in the presence of air. Such improvement comprises providing as a fuel used in such process a hydrocarbonaceous middle distillate fuel having a sulfur content of less than 500 ppm (preferably 100 ppm or less and most preferably no more than 60 ppm) and having dissolved therein a minor emission-reducing amount of (i) at least one organic nitrate combustion improver, and (ii) at least one tertiary alkyl peroxy alkanoate or peroxy benzoate of the formula



50 wherein R is a tertiary alkyl group of 4 to 8 carbon atoms and R' is an aliphatic or aromatic hydrocarbon group having 1 to 24 carbon atoms and wherein the organic nitrate combustion improver comprises a nitrate ester of a substituted or unsubstituted aliphatic or cycloaliphatic alcohol.

Still another embodiment of this invention provides improvements in the production of hydrocarbonaceous middle distillate fuels. Such improvements provide controlling or reducing the sulfur content of the fuel to a level of 500 ppm or less (preferably 100 ppm or less and most preferably no more than 60 ppm) and blending with the resultant reduced sulfur-containing fuel, (i) at least one organic nitrate combustion improver, and (ii) at least one tertiary alkyl peroxy alkanoate or peroxy benzoate of the formula



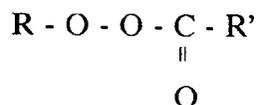
5

wherein R is a tertiary alkyl group of 4 to 8 carbon atoms and R' is an aliphatic or aromatic hydrocarbon group having 1 to 24 carbon atoms and wherein the organic nitrate combustion improver comprises a nitrate ester of a substituted or unsubstituted aliphatic or cycloaliphatic alcohol.

10

Additional embodiments of this invention involve improvements in the operation of motor vehicles and aircraft which operate on middle distillate fuels. These improvements involve fueling the vehicle or aircraft with a hydrocarbonaceous middle distillate fuel characterized by having a sulfur content of less than 500 ppm (preferably 100 ppm or less and most preferably no more than 60 ppm) and containing (i) at least one organic nitrate combustion improver, and (ii) at least one tertiary alkyl peroxy alkanoate or peroxy benzoate of the formula

15



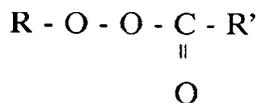
20

dissolved therein wherein R is a tertiary alkyl group of 4 to 8 carbon atoms and R' is an aliphatic or aromatic hydrocarbon group having 1 to 24 carbon atoms and wherein the organic nitrate combustion improver comprises a nitrate ester of a substituted or unsubstituted aliphatic or cycloaliphatic alcohol.

25

In accordance with a particularly preferred embodiment of this invention, there is provided a hydrocarbonaceous middle distillate fuel having a sulfur content of not more than 500 ppm (preferably 100 ppm or less and most preferably no more than 60 ppm) and a 10% boiling point (ASTM D-86) in the range of 154° to 230°C, said fuel containing a minor emission-reducing amount of (i) at least one fuel-soluble organic nitrate combustion improver, and (ii) at least one tertiary alkyl peroxy alkanoate or peroxy benzoate of the formula

30



35

wherein R is a tertiary alkyl group of 4 to 8 carbon atoms and R' is an aliphatic or aromatic hydrocarbon group having 1 to 24 carbon atoms and wherein the organic nitrate combustion improver comprises a nitrate ester of a substituted or unsubstituted aliphatic or cycloaliphatic alcohol. Such fuel compositions tend on combustion to emit especially low levels of NO_x. Without desiring to be bound by theoretical considerations, one explanation for such highly desirable performance is that fuels with higher 10% boiling points cause a delay in the progression of combustion and consequent higher peak temperatures which increase the amount of NO_x formation.

40

These and other embodiments are set forth in the ensuing description and appended claims.

45

The hydrocarbonaceous fuels utilized in the practice of this invention are comprised in general of mixtures of hydrocarbons which fall within the distillation range of about 160 to 370°C. Such fuels are frequently referred to as "middle distillate fuels" since they comprise the fractions which distill after gasoline. Such fuels include diesel fuels, burner fuels, kerosenes, gas oils, jet fuels, and gas turbine engine fuels.

Preferred middle distillate fuels are those characterized by having the following distillation profile:

50

	°F	°C
IBP	250 - 500	121 - 260
10%	310 - 550	154 - 288
50%	350 - 600	177 - 316
90%	400 - 700	204 - 371
EP	450 - 750	232 - 399

55

Diesel fuels having a clear cetane number (i.e., a cetane number when devoid of any cetane improver such

as an organic nitrate) in the range of 30 to 60 are preferred. Particularly preferred are those in which the clear cetane number is in the range of 40 to 50.

The organic nitrate combustion improvers (also frequently known as ignition improvers) comprise nitrate esters of substituted or unsubstituted aliphatic or cycloaliphatic alcohols which may be monohydric or polyhydric. Preferred organic nitrates are substituted or unsubstituted alkyl or cycloalkyl nitrates having up to 10 carbon atoms, preferably from 2 to 10 carbon atoms. The alkyl group may be either linear or branched (or a mixture of linear and branched alkyl groups). Specific examples of nitrate compounds suitable for use in the present invention include, but are not limited to, the following: methyl nitrate, ethyl nitrate, n-propyl nitrate, isopropyl nitrate, allyl nitrate, n-butyl nitrate, isobutyl nitrate, sec-butyl nitrate, tert-butyl nitrate, n-amyl nitrate, isoamyl nitrate, 2-amyl nitrate, 3-amyl nitrate, tert-amyl nitrate, n-hexyl nitrate, n-heptyl nitrate, sec-heptyl nitrate, n-octyl nitrate, 2-ethylhexyl nitrate, sec-octyl nitrate, n-nonyl nitrate, n-decyl nitrate, cyclopentyl nitrate, cyclohexyl nitrate, methylcyclohexyl nitrate, and isopropylcyclohexyl nitrate. Also suitable are the nitrate esters of alkoxy substituted aliphatic alcohols such as 2-ethoxyethyl nitrate, 2-(2-ethoxy-ethoxy)ethyl nitrate, 1-methoxypropyl-2-nitrate, and 4-ethoxybutyl nitrate, as well as diol nitrates such as 1,6-hexamethylene dinitrate. Preferred are the alkyl nitrates having from 5 to 10 carbon atoms, most especially mixtures of primary amyl nitrates, mixtures of primary hexyl nitrates, and octyl nitrates such as 2-ethylhexyl nitrate.

As is well known, nitrate esters are usually prepared by the mixed acid nitration of the appropriate alcohol or diol. Mixtures of nitric and sulfuric acids are generally used for this purpose. Another way of making nitrate esters involves reacting an alkyl or cycloalkyl halide with silver nitrate.

The concentration of nitrate ester component in the fuel can be varied within relatively wide limits with the proviso that the amount employed, when in combination with at least one tertiary alkyl peroxy alkanoate or peroxy benzoate, is at least sufficient to cause a reduction in emissions. Generally speaking, the amount of nitrate ester employed will fall in the range of 250 to 10,000 parts by weight of organic nitrate per million parts by weight of the fuel. Preferred concentrations usually fall within the range of 500 to 2000 parts per million parts of fuel.

The tertiary alkyl peroxy alkanoates or peroxy benzoates used in the practice of this invention contain at least 6 carbon atoms in the molecule, and preferably the tertiary alkyl group, R above, contains 4 to 8 carbon atoms and the hydrocarbon group, R' above, is a substantially saturated aliphatic hydrocarbon group or an unsubstituted aromatic group. The tertiary alkyl peroxy alkanoates or peroxy benzoates may be used singly with the nitrate ester component or two or more alkanoate or benzoate compounds may be used in combination with the nitrate ester component. Illustrative peroxy esters include tert-butyl peroxy-acetate, tert-butyl peroxy-butylate, tert-butyl peroxy-hexanoate, tert-butyl peroxy-heptanoate, tert-butyl peroxy-octanoate, tert-butyl peroxy-decanoate, tert-butyl peroxy-dodecanoate, tert-butyl peroxy-tetradecanoate, tert-butyl peroxy-hexadecanoate, tert-butyl peroxy-octadecanoate, tert-butyl peroxy-icosanoate, tert-butyl peroxy-tetracosanoate, tert-butyl peroxy-hexadecenoate, tert-butyl peroxyoctadecenoate, tert-butyl peroxy-2-methylhexanoate, tert-butyl peroxy-3-methylhexanoate, tert-butyl peroxy-2-ethylhexanoate, tert-butyl peroxy-2-octyloctanoate, tert-butyl peroxy-2,7-dimethyloctanoate, tert-butyl peroxy-benzoate and like compounds in which the tertiary alkyl group is tert-alkyl, 1,1,2-trimethylpropyl, 1,1,3,3-tetra-methyl-butyl or the like.

The base fuel will normally contain an amount in the range of 100 to 50,000 and preferably, from 500 to 2,000 -- parts of the tertiary alkyl peroxy alkanoate or peroxy benzoate component per million parts by weight of the base fuel (ppm). Such quantities are normally sufficient, when in combination with a substantially similar amount of organic nitrate combustion improver, to reduce the amount of diesel emission as compared to amount of emission that occurs in the same engine operated under the same conditions on the same fuel composition absent the emission-reducing additive of this invention.

Other additives may be included within the fuel compositions of this invention provided they do not adversely affect the exhaust emission reductions achievable by the practice of this invention. Thus use may be made of such components as organic peroxides and hydroperoxides, corrosion inhibitors, antioxidants, anti-rust agents, detergents and dispersants, friction reducing agents, demulsifiers, dyes, inert diluents, and like materials.

The advantages achievable by the practice of this invention were demonstrated in a sequential series of engine tests in which a Detroit Diesel 11.1 liter Series 60 engine mounted to an engine dynamometer was used. The system was operated on the "EPA Engine Dynamometer Schedule for Heavy-Duty Diesel Engines" set forth at pages 810-819 of Volume 40, Part 86, Appendix I, of the Code of Federal Regulations (7-1-86). In these tests, the first of nine consecutive tests involved operation of the engine on a conventional DF-2 diesel fuel having a nominal sulfur content in the range of 2000 to 4000 ppm. this test served as one of two baselines. In the next operation the engine was run using a low-sulfur diesel fuel having the following characteristics:

	Sulfur, ppm	50
	Gravity, API @ 60°F	34.7
5	Pour Point, °F	-5
	Cloud Point, °F	8
	Copper Strip	1
10	Distillation, °F	
	IBP	332
	10%	430
	50%	532
15	90%	632
	EP	634
	Cetane Number	44.3
20	Viscosity @ 40°C, cS	2.96

In the third and fourth tests this same low-sulfur fuel was used except that it had blended therein a diesel ignition improver composed of 2-ethylhexyl nitrate. In the third test the concentration was 2000 ppm of the organic nitrate. In the fourth test, the fuel contained 5000 ppm of the organic nitrate. The fifth involved another baseline run using the initial conventional DF-2 diesel fuel. In the sixth test another unadditized low sulfur fuel was run. The same low sulfur fuel was run in the seventh test except that the fuel contained 1250 ppm of the organic nitrate and 1250 ppm of the peroxy ester (tert-butyl peroxy-2-ethylhexanoate). In the eighth test a different unadditized low sulfur fuel was run. The ninth and final test contained the same fuel as in run eight, except that it contained 500 ppm of the organic nitrate and 500 ppm of the peroxy ester. In all instances the quantities of NO_x, unburned hydrocarbons ("HC"), carbon monoxide ("CO") and particulates emitted by the engine were measured and integrated. The results of these tests are summarized in the following table. The values shown therein for NO_x, HC, CO, and particulates, are presented in terms of grams per brake horsepower per hour. Thus the lower the value, the lower the rate and amount of emissions.

Test No.	NO _x	HC	CO	Particulates
1	4.641	0.086	1.414	0.227
2	4.345	0.068	1.490	0.165
3	4.173	0.051	1.312	0.164
4	4.208	0.073	1.324	0.165
5	4.623	0.078	1.525	0.223
6	4.270	0.224	1.600	0.153
7	4.220	0.141	1.290	0.156
8	4.350	0.157	1.480	0.154
9	4.310	0.114	1.290	0.170

In particularly preferred embodiments of this invention, use of fuels having certain boiling characteristics as well as low sulfur levels, results in still further reductions in either NO_x or particulate emissions. Thus by use of fuels meeting the low sulfur parameters set forth hereinabove and additionally having a 10% boiling point (ASTM D-86) in the range of 154° -230°C, the emissions of NO_x can be reduced to extremely low levels. Likewise, by use of fuels meeting the low sulfur parameters set forth hereinabove and additionally having a 90% boiling point (ASTM D-86) in the range of 260°-320° C, particulate emissions tend to be reduced to especially low levels. To illustrate, a Detroit Diesel Corporation Series 60 Engine in the 11.1 liter configuration and nominally rated at 320 hp at 1800 rpm was used in a series of emission tests. The engine was installed in

a heavy-duty transient emission cell equipped with a constant volume sampler (CVS) system. A dilution tunnel permitted measurements of HC, CO, NO_x and particulates according to the EPA Transient Emissions Cycle Procedure.

5 For each individual test case, the engine was started and warmed up. It was then run for 20 minutes at rated speed and load. Rated power was validated. In addition, a power test was conducted, mapping engine torque vs. speed. These parameters are required as part of the EPA Transient Cycle Procedure. Once this information was obtained, two 20-minute EPA Transient Cycles were run and engine controls were adjusted to meet statistical operating limits prescribed for the tests. The engine was shut down and allowed to soak for 20 minutes. At the end of the soak period, the Hot Start EPA Transient Cycle was run to measure NO_x, CO and particulate emissions. A second emissions evaluation was conducted after another two-minute soak. Results for the two Hot Transient Cycles were averaged into a final reported value. Whenever a fuel was changed, new fuel was introduced into the fueling system, new fuel filters were installed, and fuel lines were flushed.

10 Each fuel (A through D) was evaluated by the same Hot Start EPA Transient Emissions Cycle Procedure. Fuels A, B, and C contained 2-ethylhexyl nitrate in an amount sufficient to raise the cetane number of the respective fuels to a nominal value of 50. Fuel D which had a natural cetane number of 49.8 was used unadditized

15 Physical and chemical characterization data for unadditized fuels A through D are shown in the following table:

20

25

30

35

40

45

50

55

EP 0 537 931 A1

TABLE

Fuel Property	A	B	C	D
5 Hydrocarbon Composition, vol %				
Aromatics	36.5	28.5	37.6	39.4
Olefins	1.2	1.1	2.2	2.9
10 Saturates	62.3	70.4	60.2	57.7
Carbon, wt%	86.35	86.49	86.12	87.32
Hydrogen, wt%	13.15	13.25	12.89	13.35
15 Nitrogen, ppm	5.3	285	356	152
Sulfur, ppm	<1	225	219	476
Aniline pt., deg. C	70.1	60.0	65.4	69.4
Diene content, wt%	<0.1	0.2	<0.1	<0.1
20 Viscosity, cSt				
@ 40 deg. C	2.99	2.20	3.10	3.53
@ 100 deg. C	1.22	0.97	1.23	1.34
25 Heat of combustion BTU/lb	19,593	19,840	19,543	19,672
Boiling range, deg. C				
IBP	170	172	202	218
30 10%	217	211	234	252
20%	233	222	246	262
30%	249	230	257	271
35 40%	262	237	267	278
50%	274	244	276	284
60%	288	253	286	291
40 70%	300	263	294	298
80%	314	276	306	306
90%	331	297	322	317
45 95%	344	319	338	329
FBP	352	334	353	341
Recovery, %	98.7	98.9	98.6	98.9
Gravity, deg. API	34.9	36.1	34.6	34.5
50 Specific gravity	0.850	0.844	0.852	0.852
Calculated cetane index	48.1	44.0	48.9	51.7
Cetane index	48.5	43.8	48.3	49.7
55 Cetane number	45.3	39.6	47.7	49.8

In the above table, the following test methods were used:
Hydrocarbon composition - ASTM D-1319

4. A composition as claimed in Claim 3 wherein the organic nitrate combustion improver consists essentially of a mixture of primary hexyl nitrates.

5 5. A composition as claimed in any one of Claims 1 to 4 wherein the base fuel has a clear cetane number in the range of 30 to 60 and the following distillation profile:

	°C
IBP	121 - 260
10%	154 - 288
50%	177 - 316
90%	204 - 371
EP	232 - 399

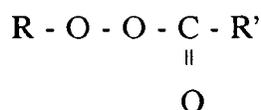
15

6. A method of reducing the amount of particulates in the exhaust of a diesel engine which comprises supplying to and burning in said engine a composition as defined in any one of Claims 1 to 5.

20

7. A combustion process wherein a middle distillate fuel is subjected to combustion in the presence of air, characterized by providing as the fuel used in such process a hydrocarbonaceous middle distillate fuel having a sulfur content of less than 500 ppm and having dissolved therein a minor emission-reducing amount of (i) at least one organic nitrate combustion improver, and (ii) at least one tertiary alkyl peroxy alkanooate or peroxy benzoate of the formula

25



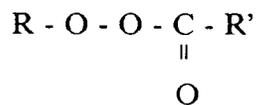
30

wherein R is a tertiary alkyl group of 4 to 8 carbon atoms and R' is an aliphatic or aromatic hydrocarbon group having 1 to 24 carbon atoms and wherein the organic nitrate combustion improver comprises a nitrate ester of a substituted or unsubstituted aliphatic or cycloaliphatic alcohol.

35

8. A process as claimed in Claim 7 wherein the combustion is effected within the combustion chamber of a compression ignition engine being operated on a diesel fuel composition composed of (i) a major proportion of a hydrocarbonaceous middle distillate fuel having a sulfur content of 100 ppm or less and a clear cetane number in the range of 30 to 60, and (ii) minor emission reducing amount of (a) at least one nitrate ester of at least one aliphatic or cycloaliphatic alcohol, and (b) at least one tertiary alkyl peroxy alkanooate or peroxy benzoate of the formula

40



45

dissolved therein wherein R is a tertiary alkyl group of 4 to 8 carbon atoms and R' is an aliphatic or aromatic hydrocarbon group having 1 to 24 carbon atoms.

50

9. A process as claimed in Claim 8 wherein the organic nitrate combustion improver consists essentially of a nitrate ester of at least one primary alkanol having 5 to 10 carbon atoms in the molecule.

55

10. A process as claimed in Claim 9 wherein the organic nitrate combustion improver consists essentially of a mixture of primary hexyl nitrates, the tertiary alkyl peroxy alkanooate is tert-butyl peroxy acetate, and the tertiary alkyl peroxy benzoate is tert-butyl peroxy benzoate.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 9066

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,X	EP-A-0 467 628 (ETHYL) * the whole document * ---	1-10	C10L1/14 C10L10/02
Y	GB-A-673 125 (STANDARD OIL) * the whole document * ---	1-3,5-7	
Y	FR-A-821 211 (BERESLAVSKY) * page 6, line 20 - line 28 * ---	1-3,5-7	
Y	US-A-2 912 313 (HINKAMP ET AL.) * column 4, line 34 - line 75 * ---	1-3,6,7	
A	DE-C-564 899 (HELMORE) * the whole document * ---	1-10	
A	FR-A-1 016 532 (JULIUS ET AL.) * the whole document * ---	1-10	
A	US-A-2 763 537 (BARUSCH ET AL.) * the whole document * ---	1-10	
A	US-A-4 330 304 (GORMAN) * the whole document * ---	1,6,7	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	US-A-2 698 512 (SCHIRMER ET AL.) * column 4, line 31 - line 71 * ---	1,2,4, 6-10	C10L
A	US-A-4 185 594 (PERILSTEIN) * the whole document * -----	1-10	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 03 NOVEMBER 1992	Examiner DE LA MORINERIE
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03.82 (P0401)