



(51) International Patent Classification:
C10L 1/10 (2006.01)

(21) International Application Number:
PCT/US2014/050763

(22) International Filing Date:
12 August 2014 (12.08.2014)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
61/869,466 23 August 2013 (23.08.2013) US

(71) Applicant: **CHEVRON U.S.A. INC.** [US/US]; 6001
Bollinger Canyon Road, San Ramon, California 94583
(US).

(72) Inventors: **NIKANJAM, Manuch**; 6001 Bollinger
Canyon Road, San Ramon, California 94583 (US).
SMAGALA, Thomas Gregory; 6001 Bollinger Canyon
Road, San Ramon, California 94583 (US).

(74) Agents: **JONES, Josetta I.** et al.; Chevron Services Com-
pany, Post Office Box 6006, San Ramon, California
94583-0806 (US).

(81) Designated States (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,

DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR,
KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME,
MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ,
OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA,
SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM,
ZW.

(84) Designated States (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a
patent (Rule 4.17(ii))*
- *as to the applicant's entitlement to claim the priority of the
earlier application (Rule 4.17(iii))*

Published:

- *with international search report (Art. 21(3))*

(54) Title: DIESEL FUEL COMPOSITION

(57) Abstract: A fuel composition is disclosed comprising a major amount of hydrocarbons boiling in the diesel range and an effective deposit-controlling amount of at least one stability additive or at least one antioxidant additive or mixtures thereof, and wherein the fuel composition contains no more than 30 ppm of active detergent additive or active dispersant additive or mixtures thereof.



DIESEL FUEL COMPOSITION

CROSS-REFERENCE TO RELATED APPLICATIONS

5 This application claims benefit under 35 U.S.C. 119 of U.S. Provisional Patent Application No. 61/869,466 with a filing date of August 23, 2013. This application claims priority to and benefits from the foregoing, the disclosure of which is incorporated herein by reference.

FIELD OF THE INVENTION

10

The present invention relates to fuel compositions. More specifically, it relates to diesel fuel compositions that contain no more than 30 ppm of active detergent additive or active dispersant additive or mixtures thereof.

15

BACKGROUND

Diesel engines have been used in applications such as stationary power generation, locomotives, ships, trucks, and automobiles. These engines, unlike gasoline engines, lack an ignition source, (i.e., spark plug) to initiate combustion in the cylinder. Air is compressed to
20 high pressure resulting in sufficiently high temperature to cause auto-ignition when diesel fuel is introduced into the combustion chamber.

Fuel injectors, therefore, are a significant element in the system to deliver fuel to the engine. Proper operation of the fuel injector is critical to the smooth operation of the engine for
25 optimum power, fuel consumption, and emissions control. Optimized operation relies on precise injection timing, fuel volume delivery, and designed spray pattern.

Diesel fuel has the tendency to form solid deposits in many engine applications at high temperature. Carbon deposits, if not controlled, build up at the injector nozzle tip and lead to
30 restricted flow volume and spray pattern. Larger fuel droplets in the combustion chamber require more time to burn efficiently. Lacking sufficient timing, fuel economy and emissions are affected adversely.

Detergent additives are commonly employed in diesel fuels to minimize or eliminate fuel injector nozzle tip carbon deposits. It has now been found that diesel engine injector deposits can be reduced or eliminated by use of diesel fuel stability and antioxidant additives.

5 SUMMARY OF THE INVENTION

The present invention is directed to a fuel composition comprising a major amount of hydrocarbons boiling in the diesel range and an effective deposit-controlling amount of at least one stability additive or at least one antioxidant additive or mixtures thereof, and
10 wherein the fuel composition contains no more than 30 ppm of active detergent additive or active dispersant additive or mixtures thereof.

The present invention is directed to a method of reducing injector deposits in a direct injection diesel engine comprising supplying a fuel composition comprising a major amount of hydrocarbons boiling in the diesel range and an effective deposit-controlling amount of at least one stability additive or at least one antioxidant additive or mixtures thereof, and wherein the fuel composition contains no more than 30 ppm of active detergent additive or active dispersant additive or mixtures thereof to an internal combustion engine.

20 The present invention further provides a fuel composition comprising a major amount of hydrocarbons boiling in the diesel range and an effective deposit-controlling amount of a fuel additive composition of the present invention.

25 The present invention also provides a method of improving the compatibility of a fuel additive composition comprising blending together the components of the fuel additive composition of the present invention.

It has been discovered that a group of diesel additives normally used as diesel fuel stabilizers and antioxidants show a surprising effect in controlling diesel fuel injector deposits normally addressed by diesel detergents. The level of deposit control is measured by power loss in an industry standard diesel engine. Such stability additives are used in fuels in many applications and also are lower in cost when compared to diesel detergents. This invention minimizes or eliminates the use of the higher cost detergent additives.

DETAILED DESCRIPTION

Definitions

- 5 The term “fuel” or “hydrocarbon-based fuel” refers to normally liquid hydrocarbons having boiling points in the range of diesel fuels.

The term “hydrocarbons boiling in the diesel range” refers to hydrocarbons having a boiling point in the range of from about 150°C to about 350°C.

10

In one embodiment, the presently claimed invention is directed to a fuel composition that may be used in a diesel engine. In one embodiment, the diesel fuel composition of the present invention has a stability additive and does not comprise a detergent additive or a dispersant additive.

15

Diesel detergent additives are used commonly to reduce or eliminate injector coking and carbon deposits. Common diesel detergent additives include, for example, aliphatic hydrocarbyl-substituted amines, hydrocarbyl-substituted poly(oxyalkylene) amines, hydrocarbyl-substituted succinimides, Mannich reaction products, nitro and amino aromatic esters of polyalkylphenoxyalkanols, polyalkylphenoxyaminoalkanes, and the like.

20

Fuels also have to be manufactured, blended, and/or additized to ensure stability. Unstable diesel fuel can degrade, undergo undesirable chemical reactions, and form solid particles. Such particles can clog fuel filters and reduce fuel flow to the engine. They also can interfere with the operation of pumps and injectors that have extremely small clearances between sliding or rotating surfaces. Stability can be thermal (engine and vehicle environment) or storage (long term).

25

Stability Additives

30

Typically, stability additives prevent oxidation and degradation of the diesel fuel. For purposes of this disclosure, stability includes, but is not limited to, thermal stability, storage stability, oxidative stability and the like. Common stability additives and antioxidants

include, but are not limited to, hydroquinone and its derivatives, alkyl phenols, various amines such as substituted phenylenediamines, and combinations of amines and phenols, either as separate molecules or bonded together in amine-phenolic resins. Amine-phenolic resin stability additives are known and are commercially available, for example, from Nalco
5 (e.g., EC5111A, EC5300A and EC5302A) and Innospec (e.g., FOA-91).

When selecting fuel additives, it is essential to ensure that additives perform well, are cost effective, and do not contribute to harmful side effects. Interaction among various types and classes of additives should be considered. As such, it is beneficial to reduce the number and
10 the concentration of diesel fuel additives.

It has been discovered that employing certain stability additives or antioxidant additives or mixtures thereof in diesel fuel, and wherein the fuel composition contains no more than 30 ppm of active detergent additive or active dispersant additive or mixtures thereof, results in
15 deposit control. Preferably, the diesel fuel contains stability additives or antioxidant additives or mixtures thereof, and the fuel composition contains no more than 20 ppm of active detergent additive or active dispersant additive or mixtures thereof.

Fuel Compositions

20

The stability additive will generally be employed in a hydrocarbon distillate fuel. The proper concentration of additive necessary in order to achieve the desired deposit control varies depending upon the type of fuel employed and other additives employed. Generally, however, from 10 to 200 ppm weight (mg active additive/kg diesel fuel) of the active stability
25 additive (e.g., from 50 to 200, from 50 to 175, from 50 to 150, from 75 to 200, from 75 to 175, from 75 to 150, from 100 to 200, from 100 to 175, or from 100 to 150 ppm weight (mg active additive/kg diesel fuel) of the active stability additive) is needed to achieve the best results.

30 In diesel fuels, other well-known additives can be employed, such as pour point depressants, cold flow improvers, lubricity improvers, cetane number improvers, conductivity improvers and the like.

The diesel fuels employed with the stability additive of the present invention include finished diesel fuels where levels of sulfur, aromatics, and paraffins range from typical amounts to only trace amounts. In a further embodiment, the diesel fuel has a high concentration of sulfur. Specifically, the sulfur content is from about 0 to about 5000 ppm weight sulfur.

5

Engine Performance

Using vehicles in service to evaluate engine performance due to formation of carbon deposits in injector nozzle tips is not practical. It is common practice for such evaluations to develop
10 laboratory tools which have been correlated with vehicles on the road and have been verified by credible standard setting groups.

Two such tools have been developed by the Coordinating European Council (CEC), and used broadly by research laboratories.

15

One such tool is a DW-10 engine on a test stand (CEC F-98-08). This is a two-liter four-cylinder in-line overhead camshaft turbocharged engine with EGR. This more modern direct injection engine is equipped with a common rail system for fuel delivery. The test procedure was developed to discriminate among fuels that vary in their ability to produce injector
20 deposits in Euro V passenger car direct injection diesel engines. The level of injector deposit formation is indicated by the power loss in a well-defined test cycle and test procedure.

A second evaluation tool is the XUD-9 engine on a test stand (CEC F-23-01). This is an indirect injection system representing the older diesel engines in service. It lacks the modern
25 common rail injection system. It is a four-cylinder 1.9 liter engine fitted with clean fuel injectors at the start of the test. After operating for ten hours with a prescribed cycle, the tendency of the fuel to generate injector deposits is determined by the percent flow loss at a needle lift of 0.10 mm.

30 Proper operation of diesel equipment requires diesel fuel meeting several performance categories and physical and chemical properties including, but not limited to, the specifications in ASTM D975, Standard Specification for Diesel Fuel Oils. Fuel properties and considerations include, but are not necessarily limited to, the following possible

categories: cetane number, lubricity, stability, conductivity, deposit control, cleanliness, low temperature operation, density, and flash point. Many of these and other properties can be controlled by refinery processes, blending options, and/or use of chemical additives, to result in a fuel that is fit for purpose.

5

EXAMPLES

The following examples are intended to be non-limiting.

10 In one experiment, it was attempted to define the required amount of detergent additive for a fuel. This fuel was one that required a stability additive. The test matrix required testing the finished fuel (i.e., a fuel containing additives such cetane number improvers, lubricity additives and the like as listed herein above) both with and without detergent to establish a baseline and to demonstrate the benefit of using the detergent additive. Testing the stabilized
15 finished fuel without detergent additive resulted in very little power loss in the DW-10 engine, indicating very little generation of carbon deposits. Power loss level was low and very similar, both with and without the detergent additive. It was surprising to observe that the stability additive worked to restore power without the use of the deposit control additive. Similar testing using the XUD-9 engine also resulted in a surprising benefit.

20

Based on this discovery, it is now possible to reduce or eliminate the use of detergent additive and still maintain low injector deposits resulting in optimum performance.

A test program was conducted to utilize engine testing to evaluate two types of fuel, those
25 containing high and low amounts of sulfur, with and without a detergent additive (TECHRON[®] D), in a statistically designed randomized test matrix. Finished diesel fuels with higher levels of sulfur (i.e., greater than 15 ppmw sulfur) required a stability additive to prevent degradation. The results of the CEC F98-08 DW-10 engine tests are set forth in Table 1.

30

TABLE 1
CEC F-98-08 DW-10 Engine Test Results

Example	Base Fuel	Detergent Additive	Stability Additive	Amount of Stability Additive	Power Loss (%)
1	S5000	Yes	Yes (FOA-91)		0.39
2	S5000	Yes	Yes		0.67
3	S5000	No	Yes (FOA-91)		1.88
4	S5000	No	Yes (FOA-91)		3.18
5	S15	Yes	No		2.45
6	S15	Yes	No		2.63
7	S15	No	No		9.38
8	S15	No	No		9.42
9	S15	No	Yes (FOA-91)		4.72
10	S15	No	Yes (EC5300A)		3.05
11	S15 (CARB)	No	No		7.83
12	S15 (CARB)	No	Yes (BHT)	180 ppm	8.73
13	S15 (CARB)	No	Yes (EC5111A)	150 ppm	2.61
14	S15 (CARB)	No	Yes (EC5302A)	150 ppm	3.34

5

The diesel fuels presented in the Tables herein represent classes of diesel fuels as characterized according to ASTM D975, i.e., S15 = maximum 15 ppm sulfur and S5000 = maximum 5000 ppm sulfur.

- 10 The initial tests under the DW-10 testing environment using high sulfur diesel with detergent additive resulted in very little power loss (0.39%) as expected. Lower sulfur diesel with detergent additive also resulted in small power loss (2.45%) as expected. The same fuel without detergent additive resulted in significant power loss (9.38%). When higher sulfur diesel fuel without detergent additive was tested, it was surprising to notice very little power loss (1.88%). This condition was repeated with the same surprising result, a low power loss (3.18 %).

To confirm the integrity of the engine operation, the lower sulfur fuel requiring no stability additive was tested without detergent additive and resulted in an expected high power loss (9.42%). This was followed by a test of the same lower sulfur fuel without stability additive but with detergent additive. Low power loss (2.63%) resulted as expected.

Although the lower sulfur fuel is naturally stable and requires no stability additive, stability additive was added to the fuel for engine testing without use of a detergent. Surprisingly, lower power loss (4.72%) resulted.

5

For additional verification, another type of diesel fuel stability additive (amine –phenolic resin, Nalco EC5300A) was added to the lower sulfur fuel for engine testing. Once again, power loss was low (3.05%) when no detergent was used. This indicated that stability additive could keep injectors clean in a similar manner to what is expected of a diesel
10 detergent.

Three other stability additives were tested in a lower sulfur CARB fuel without detergent. Again, the fuel without detergent and without stability additive resulted in higher power loss (7.83%). One additive (BHT) was not effective resulting in high power loss (8.73%). Two
15 stability additives were effective in keeping injectors clean and resulting in lower power losses (2.61% and 3.34%).

Parallel testing was performed using the second industry standard test engine, XUD-9. Fuel cleanliness with respect to injector deposits is measured upon completion of a 10-hour test by
20 determining percent flow restriction due to formation of nozzle tip deposits. The results of the CEC F98-08 XUD-9 F-23-01 engine tests are set forth in Table 2 below.

TABLE 2
CEC F-23-01 XUD-9 Engine Test Results

Example	Base Fuel	Detergent	Stability Additive	% Plugged
15	S5000	Yes	Yes (FOA-91)	60
16	S5000	Yes	Yes (FOA-91)	60.9
17	S5000	No	Yes (FOA-91)	62
18	S5000	No	Yes (FOA-91)	57
19	S15	Yes	No	11
20	S15	Yes	No	11.4
21	S15	No	No	76
22	S15	No	No	81.5
23	S15	No	Yes (FOA-91)	40.3

25

Higher sulfur diesel fuel had about the same level of flow restriction without detergent (57%) and with detergent (60%) indicating that the stability additive in the fuel was performing the same as the detergent. This was repeated for confirmation with same result, 62% without detergent vs. 61% restriction with the detergent.

5

Lower sulfur diesel fuel which does not require a stability additive was tested without detergent twice, resulting in high flow restrictions of 76% and 81.5%. This fuel without stability additive was tested with detergent and resulted in much lower flow restriction of 11% and 11.4%. This indicates that when stability additive is not present, the nozzle flow restriction is noticeable with the use of a detergent.

10

WHAT IS CLAIMED IS:

1. A fuel composition comprising a major amount of hydrocarbons boiling in the diesel range and an effective deposit-controlling amount of at least one stability additive or at least one antioxidant additive or mixtures thereof, and wherein the fuel composition contains no more than 30 ppm of active detergent additive or active dispersant additive or mixtures thereof.
2. The fuel composition according to claim 1, wherein the fuel composition contains no more than 20 ppm of active detergent additive or active dispersant additive or mixtures thereof.
3. The fuel composition according to claim 1, wherein the fuel composition contains about 10 to 200 weight ppm of the stability additive.
4. The fuel composition according to claim 3, wherein the fuel composition contains about 100 to 200 weight ppm of the stability additive.
5. The fuel composition according to claim 1, wherein the stability additive is an amine-phenolic resin.
6. A method of reducing injector deposits in a direct injection diesel engine comprising supplying a fuel composition comprising a major amount of hydrocarbons boiling in the diesel range and an effective deposit-controlling amount of at least one stability additive or at least one antioxidant additive or mixtures thereof, and wherein the fuel composition contains no more than 30 ppm of active detergent additive or active dispersant additive or mixtures thereof to an internal combustion engine.
7. The method according to claim 6, wherein the fuel composition contains no more than 20 ppm of active detergent additive or active dispersant additive or mixtures thereof.
8. The method according to claim 6, wherein the fuel composition contains about 10 to 200 weight ppm of the stability additive.

9. The method according to claim 8, wherein the fuel composition contains about 100 to 200 weight ppm of the stability additive.
- 5 10. The method according to claim 6, wherein the stability additive is an amine-phenolic resin.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 14/50763

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C10L 1/10 (2014.01)

CPC - C10L 1/06; C10L 1/08; C10L 1/1608

According to International Patent Classification (IPC) or to both: national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC C10L 1/10 (2014.01)

CPC C10L 1/06; C10L 1/08; C10L 1/1608

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC 44/300,309 (Keyword limited, terms below)Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase, Google Patents, Google Scholar (NPL); Keywords: fuel composition diesel additive antioxidant dispersant detergent amine phenolic

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005/0160662 A1 (Jordan) 28 July 2005 (28.07.2005) para [0103]-[0104], [0115]-[0116]	1-2, 5-7, 10
Y		3-4, 8-9
Y	US 2012/0103290 A1 (Startin et al.) 03 May 2012 (03.05.2012) para [0003], [0015], [0060], [0067], [0067]	3-4, 8-9
A	US 2004/0168364 A1 (MacDuff et al.) 02 September 2004 (02.09.2004) entire document	1-10

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

15 October 2014 (15.10.2014)

Date of mailing of the international search report

05 DEC 2014

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-3201

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774