(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
8 April 2010 (08.04.2010)

PCT

(10) International Publication Number
WO 2010/039282 A1

(51) International Patent Classification:
C10L 1/18 (2006.01) *C08G 8/04* (2006.01)

(21) International Application Number:
PCT/US2009/039173

(22) International Filing Date:
1 April 2009 (01.04.2009)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
12/243,753 1 October 2008 (01.10.2008) US
12/246,057 6 October 2008 (06.10.2008) US

(71) Applicant *(for all designated States except US)*: **BAKER HUGHES INCORPORATED** [US/US]; P.o. Box 4740, Houston, TX 77027 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **STARK, Joseph, L.** [US/US]; 3538 Timothy Lane, Richmond, TX 77469 (US). **JOHNSON, Koral, B.** [US/US]; 4119 San Augustine Avenue, Pasadena, TX 77503 (US).

(74) Agent: **LITTLEFIELD, Stephen, A.**; Baker Petrolite Divison-baker Hughes Incorporated, Division Intellectual Property Counsel, P.O. Box 4740, Houston, TX 77027 (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, BR, BW, BY, BZ, CA, CH, 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, IS, JP, KE, KG, KM, 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, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, 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, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (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, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

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

WO 2010/039282 A1

(54) **Title**: FUEL ADDITIVE USEFUL FOR INCREASING HORSEPOWER

(57) **Abstract**: Alkylphenol resins, either with or without components selected from the group consisting of fatty acid amides, mannich resins and mixtures thereof; are effective additives for increasing the horsepower of fuel oils. The additives may also simultaneously improve emission performance. It is emphasized that this abstract is provided to comply with the rules requiring an abstract which will allow a searcher or other reader to quickly ascertain the subject matter of the technical disclosure. It is submitted with the understanding that it will not be used to interpret or limit the scope or meaning of the claims. 37 CFR 1.72(b)

FUEL ADDITIVE USEFUL FOR INCREASING HORSEPOWER

Inventors: **Joseph L. Stark**
Koral B. Johnson

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to fuel additives. The present invention particularly relates to fuel additives useful for increasing horsepower.

2. Background of the Art

[0002] Historically, fuel oils, also known as heavy fuel oils, have been considered to be those compounds resulting from the refining of crude oil having a vapor pressure at ambient too low to allow for easy combustion. If it could be heated and pumped, it was considered a fuel oil and used in engines that could burn such heavy fuels. Exemplary applications included marine engines, locomotive engines, turbines, and use in boilers such as those oils used for power generation.

[0003] More recently, fuel oil may include those coming from other sources, both synthetic and non-synthetic. For example, one synthetic source fuel oil is the so called Fischer-Tropsch fuels. Fischer-Tropsch fuels, also known as FT fuels, include those described as gas-to-liquid (GTL) fuels, biomass-to-liquid (BTL) fuels and coal conversion fuels. To make such fuels, syngas (CO + H (2)) is first generated and then converted to normal paraffins by a Fischer-Tropsch process. The normal paraffins may then be modified by processes such as catalytic cracking/reforming or isomerisation, hydrocracking and hydroisomerisation to yield a variety of hydrocarbons such as iso-paraffins, cyclo-paraffins and aromatic compounds. The resulting FT fuel can be used as such or in combination with other fuel components and fuel types such as those mentioned elsewhere in the specification.

[0004] Even fuels derived from natural sources such as bio-diesels and plant oils may result in the production of at least some heavy fuel oils.

[0005] Whatever their source, fuels oils today are the subject of specifications due to the requirements of both governmental regulations and less forgiving apparatus for using the fuel oils. It may be desirable in the art to produce fuel oils that meet such specifications and also have improved horsepower in comparison to conventional fuel oils.

SUMMARY OF THE INVENTION

[0006] In one aspect, the invention is an additive for increasing the horse power of fuel comprising at least a first component which is an alkylphenol resin.

[0007] In another aspect, the invention is an additive for increasing the horsepower of fuel comprising at least a first component which is an alkylphenol resin and further comprising a second component selected from the group consisting of a fatty acid amide, a mannich resin and mixtures thereof.

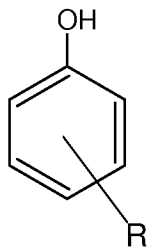
[0008] In still another aspect, the invention is a method for increasing the horsepower of an engine burning a fuel comprising admixing a fuel with an additive comprising at least a first component which is an alkylphenol resin and using that fuel to power the engine.

[0009] Another aspect of the invention is an admixture of a fuel and an additive for increasing the horsepower of fuels, the additive comprising at least a first component which is an alkylphenol resin.

Description of the Preferred Embodiments

[0010] In one embodiment, the present invention is an additive useful for increasing the horsepower of a fuel. Horsepower is a measurement of the force exerted by an engine. It has been defined as a unit of power in the U.S. Customary System, equal to 745.7 watts or 33,000 foot-pounds per minute. For the purposes of this application, the phrase "increasing the horsepower of a fuel" is defined to mean "increasing the power output of an engine powered by a fuel of the disclosure as compared to the output of the same engine powered by a conventional, but otherwise identical fuel."

[0011] The additives useful for creating this increase in horsepower are those comprising at least a first component which is an alkylphenol resin. The alkyl phenol resins useful as the first component of the additives of the invention include those prepared by reacting an alkyl phenol with an aldehyde. The alkyl phenol may be nonyl phenol but other alkyl phenols may be used. Exemplary alkyl phenols useful for preparing the alkyl phenol resin of the invention include those having the general formula:



wherein R is an alkyl group having from 4 to 18 carbons.

[0012] The alkyl phenol resin may be prepared by reacting the alkyl phenol with an aldehyde. Aldehydes useful for preparing the alkyl phenol resins include formaldehyde, but higher aldehydes may also be used. Higher aldehydes which may be used to prepare the alkyl phenol resins include those aldehydes having from 2 to about 5 carbons.

[0013] The alkyl phenol resins may have a molecular weight (M_w) of from about two thousand to about twenty five thousand Daltons. In one embodiment, the alkyl phenol resin has a molecular weight of from about four to about twenty thousand Daltons. In still another embodiment, the alkyl phenol resin has a molecular weight of from about five to about ten thousand Daltons. While the structure of the alkyl phenol resins useful with the invention has been described as the reaction product certain starting materials, the alkyl phenol resins may be prepared by any means known to those skilled in art to be useful for preparing such resins.

[0014] In another embodiment, the additives of the invention may also include a second component selected from the group consisting of fatty acid amides, mannich resins and mixtures thereof. The fatty acid amides useful with the invention include those prepared using a fatty acid having from 8 to about 26 carbons. The amides may be prepared using a hydroxyl alkyl amine such as 2-(2-amino ethylamine) ethanol, diethanolamine, or aminoethyl ethanolamine or other hydroxyl alkyl amine having from about 4 to about 8 carbons. While the structure of the fatty acid amides useful with the invention has been described as the reaction product certain starting materials, the fatty acid amides may be prepared by any means known to those skilled in art to be useful for preparing such resins.

[0015] Mannich resins useful with the invention include those which may be prepared using an alkyl phenol, an aldehyde and a polyamine. The alkyl phenols useful in preparing the Mannich resins include those already described above, namely those phenols also having an alkyl group on the aromatic ring having from about 4 to about 36 carbons. For example dodecyl phenol may be used to prepare the Mannich resins useful with the invention.

[0016] Similarly the Mannich resins useful with the invention include those made

made with formaldehyde but may also include those prepared with higher aldehydes. Higher aldehydes which may be used to prepare the Mannich resins include those aldehydes having from 2 to about 5 carbons.

[0017] The polyamines useful for preparing the mannich resins include ethylene diamine, but other amines may also be used. Any amine having at least two amino groups and from 2 to 22 carbons may be used to prepare the Mannich resins.

[0018] The Mannich resins may have a molecular weight (M_w) of from about two thousand to about twenty five thousand Daltons. In one embodiment, the Mannich resin has a molecular weight of from about four to about twenty thousand Daltons. In still another embodiment, the Mannich resin has a molecular weight of from about five to about ten thousand Daltons. While the structure of the Mannich resins useful with the invention has been described as the reaction product certain starting materials, the Mannich resins may be prepared by any means known to those skilled in art to be useful for preparing such resins.

[0019] The additives of the disclosure may be admixed with fuel oils using any method known by those of ordinary skill in the art to be useful. For example, in one embodiment, the additives are admixed with fuel oils when the fuel oils are being prepared by admixing oils of varying viscosity to achieve a target viscosity. In another embodiment, the additives are admixed when the fuel oils being subjected to treatment are being metered into a truck, ship or other vessel.

[0020] The actual means of admixing a fuel oil with an additive of the invention may include any apparatus useful for same. Exemplary apparatus include static mixers, blade mixers, stirred vessels, vessels having recycles lines incorporating static or blade mixers and the like. Any apparatus for mixing known to be useful to those of ordinary skill in the art may be used with the method of the invention. Passive

with the method of the invention. Passive admixing may be accomplished where the additives are introduced into a vessel or transfer line or pipeline and admixing is effected by means of turbulence.

[0021] The concentration of the additives needed to increase the horsepower of a given fuel will vary depending upon the properties of the subject fuel. Still, in at least one embodiment, the method of the invention may be practiced by admixing sufficient additive to achieve a concentration of from 10 to about 3000 ppm (by weight) of additive in the fuel being treated. In other embodiments, the concentration is from about 10 to 2000 ppm. In still other embodiments, the concentration is from about 50 to about 1000 ppm.

[0022] The additives of the invention may be used with any fuel. The fuels which are most likely to need the additives of the invention are those characterized as having a boiling point greater than about 104°F (40°C). These include heavy fuel oils which are often used as fuel in marine engines and locomotives. Such heavy oils are often also used for firing boilers for electricity generation or steam generation. Any fuel capable of being used in a compression engine may be improved using the additives of the disclosure to increase the horsepower of an engine employing the fuel.

[0023] Generally, an improvement in horsepower of an engine is accompanied by a degradation of emissions parameters. In some embodiments, the additives of the disclosure may be employed to increase horsepower with negligible degradation of emission parameters. In some embodiments, the emissions of an engine may be improved along with horse power. Exemplary of such parameters are CO emissions, CO_2 emissions, and NO_x emissions. Improvements may also be seen in engine efficiency when additives are used in the fuel.

EXAMPLES

[0024] The following examples are provided to illustrate the invention. The examples are not intended to limit the scope of the invention and they should not be so interpreted. Amounts are in weight parts or weight percentages unless otherwise indicated.

Example 1

[0025] A fuel was prepared by admixing a first oil having the properties listed in the table below with an Ultra Low Sulfur Diesel in a ratio of 86.5:13.5 to prepare a fuel having a viscosity of 183 cSt at 50 °C. The first oil had an asphaltenes concentration of 8.5%, a sulfur content of 2.65%, an API gravity value of 12.8 and a specific gravity of 0.9806. The Ultra Low Sulfur Diesel had an API gravity value of 33.4 and specific gravity of 0.8581.

[0026] The additive is prepared using the components shown in the Table. The alkyl phenol resin is an alkyl phenol resin prepared using nonyl phenol and formaldehyde and has a molecular weight (M_w) of 2000 to 5000 g/mole done using a GPC and polystyrene standard. The Mannich resin is prepared using dodecyl phenol, formaldehyde and ethylene diamine. It has a molecular weight similar to that of the alkyl phenol resin. The fatty acid amide is prepared using a C_{18} fatty acid and aminoethyl ethanol amine.

Example 2

[0027] Additive 1-4 was tested for its ability to improve the horsepower of a fuel oil. The testing was conducted using a Detroit Diesel (8V-921A) 560 BHP engine, with Marine Diesel Oil (MDO) having 500 ppm of the additive, the engine being used to pump pressurized water. The experiments were conducted at 2000 RPM and water

conducted at 2000 RPM and water pressure ~4000 PSI. Horsepower for the engine was calculated based on the measured flow rate of the pressurized water.

[0028] The emissions were monitored using a Mobile Emissions Tester, which monitored the following real time parameters: CO concentration, NO concentration, NO_2 concentration, O_2 concentration, exhaust temperature, and exhaust flow rate. Combustion efficiency and CO_2 concentration were calculated based on various thermodynamic formulas. All horsepower and emission measurements were conducted with the following protocol:

Step 1: 5 minutes warm up on idle;
Step 2: 4 minutes of running at 2000 RPM;
Step 3: Turn on the Load;
Step 4: 1 minutes of running with Load switched on;
Step 5: Turn on the Mobile Emissions Tester;
Step 6: 20 minutes of continuous monitoring of BHP and emissions;
Step 7: Turn off the BPC mobile emissions tester;
Step 8: Turn off the load;
Step 9: Turn off the engine for 20 minutes for cooling for period; and
Step 10: Repeat step 1-9 to check for reproducibility.

[0029] The fuel and additive is compared to a blank with the following results:

Average % Horsepower increase: 2.7

Maximum % Horsepower Increase: 4.6

Average % Increase in Engine Efficiency: 2.4

Maximum % Increase in Engine Efficiency: 4.4

Increase in Engine Temperature: 0

Change (%) in Exhaust Temperature: -0.6

Change in CO Emissions (%): -6.9

Change in CO_2 Emissions (%): -0.9

Change in NO_x Emissions (%): +0.1

Table

Sample	Alkylphenol [%]	Mannich Res [%]	Fatty Acid Amide [%
1-1	100	0	0
1-2	60	40	0
1-3	60	0	40
1-4	60	20	20

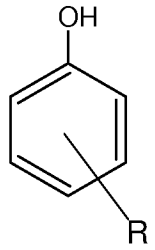
Brief Discussion of the Examples

[0030] The Examples illustrate that the additive of the disclosure was useful in increasing generally the horsepower of an engine as compared to running the engine with an untreated fuel. Surprisingly, the horsepower improvements were noted with a general improvement in the emissions characteristics of the engine.

WHAT IS CLAIMED IS:

1. An additive for increasing horsepower in fuel comprising at least a first component which is an alkylphenol resin.

2. The additive of Claim 1 wherein the alkyl phenol resin is prepared using an alkyl phenol having a general formula:



wherein R is an alkyl group having from 4 to 18 carbons.

3. The additive of Claim 2 wherein the alkylphenol is reacted with formaldehyde to form the alkylphenol resin.

4. The additive of Claim 1 wherein the alkylphenol resin has a molecular weight (M_w) of from about 3,000 to about 20,000 Daltons.

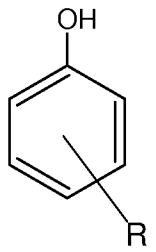
5. The additive of claim 1 further comprising a second component selected from the group consisting of a fatty acid amide, a mannich resin and mixtures thereof.

6. The additive of Claim 5 wherein the second component is a fatty acid amide having from about 8 to about 26 carbons.

7. The additive of Claim 6 wherein the fatty acid amide is prepared using a compound selected from the group consisting of 2-(2-amino ethylamine)ethanol, diethanolamine, aminoethyl ethanolamine and mixtures thereof.

8. The additive of Claim 5 wherein the second component is a mannich resin prepared from a formulation including an alkyl phenol, an aldehyde and a polyamine.

9. The additive of Claim 8 wherein the alkyl phenol has a general formula:



wherein R is an alkyl group having from 4 to 18 carbons.

10. The additive of Claim 9 wherein the alkyl phenol is dodecyl phenol.

11. The additive of Claim 8 wherein the aldehyde is formaldehyde.

12. The additive of Claim 8 wherein the polyamine has from 2 to 22 carbons.

13. The additive of Claim 12 wherein the polyamine is ethylene diamine.

14. The additive of Claim 5 wherein the second component is a mannich resin having a molecular weight (M_w) of from about from about 4,000 to about 20,000 Daltons.

15. A method for increasing horsepower of a fuel comprising admixing a fuel oil with an additive comprising at least a first component which is an alkylphenol resin.

16. The method of Claim 15 wherein the additive additionally comprises a second component selected from the group consisting of a fatty acid amide, a mannich resin and mixtures thereof.

17. The method of Claim 15 wherein the additive is admixed with the fuel at a concentration of from about 10 to about 3,000 ppm.

18. The method of Claim 17 wherein the additive is admixed with the fuel at a concentration of from about 50 to about 1,000 ppm.

19. A composition comprising an admixture of a fuel and an additive of Claim 1.

20. The composition of Claim 19 wherein the fuel has a boiling point greater then 104˚F (40℃)

21. The composition of Claim 20 wherein the fuel is a heavy fuel oil.

22. The composition of Claim 21 wherein the heavy fuel oil is Bunker C oil.

23. The composition of Claim 19 wherein the additive is present at a concentration of from about 10 to about 2,000 ppm.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 09/39173

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C10L 1/18; C08G 8/04 (2009.01)
USPC - 44/385; 528/165
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(8) -- C10L 1/18; C08G 8/04 (2009.01) and USPC -- 44/385; 528/165

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
IPC(8) -- C10L$ (2009.01) and USPC -- 44/351,354,385,443; 528/165; 508/306

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWest (PGPB,USPT,EPAB); USPTO; Espacenet; Google Patents; Google Scholar; Google -- ALKLYPHENOL; ALKYL PHENOL; BUNKER OIL; DIESEL; DIETHANOLAMINE; DODECYLPHENOL; FATTY ACID AMIDE; FORMALDEHYDE; FUEL OIL; HORSEPOWER; MANNICH; NONYLPHENOL; OCTYLPHENOL; PHENOL; POWER; RESIN

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2005/0166447 A1 (Corkwell et al.) 04 August 2005 (04.08.2005) para [0005]; [0010]; [0015]; [0023]; [0025]; [0026]; [0028]; [0032]; [0038]	1-3,5-13,15-20,23 --- 4,14,21,22
Y	US 4,553,979 A (Hanlon et al.) 19 November 1985 (19.11.1985) col 1, ln 5-11; col 3, ln 1-10	4,14
Y	US 2003/0226312 A1 (Roos et al.) 11 December 2003 (11.12.2003) para [0028]	21,22

☐ 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	Date of mailing of the international search report
13 May 2009 (13.05.2009)	26 MAY 2009
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

Form PCT/ISA/210 (second sheet) (April 2007)