

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

**(19) World Intellectual Property Organization
International Bureau**



**(43) International Publication Date
13 September 2001 (13.09.2001)**

PCT

(10) International Publication Number
WO 01/66674 A1

(51) International Patent Classification⁷: C10L 1/06

[GB/GB]; 19 Varsity Place, John Towle Close, Oxford OX1 4TZ (GB). **SCHILOWITZ, Alan, Mark** [US/US]; 15 N. Sixth Avenue, Highland Park, NJ 08904 (US).

(22) International Filing Date: 8 March 2001 (08.03.2001)

(74) **Agents:** DEW, Melvyn, John et al.; ExxonMobil Chemical Europe Inc., P.O. Box 105, B-1830 Machelen (BE).

(25) Filing Language: English

(26) Publication Language: English

(61) Designated States (*national*): CA, HI, SG, US.

(30) Priority Data: 0005936.0 10 March 2000 (10.03.2000) GB

(84) Designated States (regional): European patent (A1, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).

(71) **Applicant (for all designated States except US): EXXON-MOBIL RESEARCH AND ENGINEERING COMPANY [US/US]; 1545 Route 22 East, Clinton Township, Annandale, NJ 08801 (US).**

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

(72) Inventors; and

(75) **Inventors/Applicants (for US only): BARBOUR, Robert, Howie [GB/GB]; 12 Elport Close, Hulland Ward, Ashbourne, Derby DE6 3FR (GB). PACE, Stuart**

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

卷之三

WO 01/66674 A1

(54) Title: FUEL COMPOSITION

(57) Abstract: A fuel composition comprising gasoline having a sulphur content of less than 10 ppm by weight and an aromatic content of less than 25 % by volume, characterized in that said composition comprises at least 5 % by volume of olefins and is substantially free of any ethers. The fuel composition so formed has reduced emissions and improved fuel economy. The emissions from such compositions can be further reduced by incorporating therein a small amount of ethanol.

FUEL COMPOSITION

This invention relates to fuel compositions of ultra-low sulphur and low aromatics content which have improved friction properties and hence adequate lubricity thereby having 5 improved wear control and acceptable combustion performance.

Fuels such as motor gasoline are widely used in automotive transport. However, in line with the general thrust to reduce air pollution, petroleum companies and vehicle manufacturers are looking to develop systems that have reduced exhaust emissions and 10 improved fuel economy. The petroleum companies in turn are introducing fuels with low sulphur content as they are considered to be more compatible with exhaust catalyst systems. One of the methods of reducing the sulphur content is to subject the fuel to hydrotreatment. One of the problems with such fuels with relatively low sulphur content is that the reduction 15 of sulphur content also adversely affects the lubricity of the resultant fuel. For instance, low sulphur fuels may lead to premature wear in some submerged electric gasoline pumps. Low sulphur distillate fuels have also been shown to have an adverse wear effect on diesel fuel system components such as rotary fuel pumps and fuel injection systems. Moreover, improved fuel lubricity may also lead to improved fuel economy. The hydrotreatment process also reduces the olefinic content of the fuel since hydrogenation saturates the olefins 20 therein during the process of sulphur removal. Loss of olefins adversely affects the performance of gasoline since olefins are key contributors to octane performance. This drawback has been met hitherto by the use of octane improvers such as e.g. methyl tertiary butyl ether. However, the use of the latter has recently been called into question for environmental reasons and has fallen out of favour. Consequently, it is necessary to 25 formulate fuel compositions which are low in sulphur content but are also of the desired lubricity in order to minimise wear and friction when used in automotive engines. At the same time, it is desirable to retain the octane performance of the fuel. In addition to the issue of low sulphur, the presence of relatively high levels of aromatics in the fuels also adversely affect performance in that they give rise to undesirable emissions, especially of 30 hydrocarbons, and can also cause combustion chamber deposits which again exacerbates the undesirable effect on emissions. Thus, whilst improving the lubricity performance of the fuel and sufficient octane level, it is also essential to control the aromatic content thereof to meet the current and impending future regulations on exhaust emissions. Consequently, it can be difficult to simultaneously produce motor gasoline with high octane, good lubricity 35 and good emissions performance.

It has now been found that the lubricity and octane performance of ultra-low sulphur fuels can be restored whilst controlling the aromatic content thereof by increasing the olefinic content thereof without recourse to the use of ethers.

5 Accordingly, the present invention is a fuel composition comprising gasoline having a sulphur content of less than 10 ppm by weight and an aromatic content of less than 25% by volume, characterized in that said composition comprises at least 5% by volume of olefins and is substantially free of any ethers.

10 As described above, the sulphur content of the fuel composition is less than 10 ppm by weight, is preferably less than 5 ppm by weight. Such low sulphur levels can be achieved in a number of ways. The base fuels may comprise mixtures of saturated, olefinic and aromatic hydrocarbons and these can be derived from straight run streams, thermally or catalytically cracked hydrocarbon feedstocks, hydrocracked petroleum fractions, 15 catalytically reformed hydrocarbons, or synthetically produced hydrocarbon mixtures. Typically, the present invention is applicable to fuels such as the light boiling gasoline (which typically boils between 50 and 200°C), especially motor gasoline. The sulphur content of such fuels can be reduced below the 10 ppm level by well known methods such as eg, catalytic hydrodesulphurisation. The lubricity properties of ultra-low sulphur (< 10 ppm) 20 base fuels which have an aromatic content of less than 25% by volume, preferably less than 20% by volume are generally poor. These fuels particularly benefit from the presence of olefins therein in an amount of at least 5% by volume, suitably at least 10% by volume and preferably from 10-25% by volume, eg 15% by volume of the total fuel.

25 The olefins that may be used for this purpose are suitably C₃-C₁₀ mono-olefins and are preferably alpha-olefins. Thus, the olefins may be one or more selected from the group consisting of pent-1-ene, hex-1-ene, hept-1-ene, oct-1-ene, non-1-ene and dec-1-ene.

30 Fuel compositions comprising gasoline as the base fuel in general are susceptible to evaporative losses and the consequent release of volatile hydrocarbons and other organics is a cause for environmental concern. Such volatile losses can occur in distribution systems, during fuelling, during vehicle operation (running losses) and even while the vehicle is parked (diurnal losses). Such release of hydrocarbons and organics into the environment can contribute to ozone production and can be a direct source of toxic components such as e.g. benzene. The volatility of gasoline is usually quantified by the vapour pressure of the 35 gasoline composition and the industry standard is RVP (Reid Vapour Pressure) according to the so-called Setavap procedure (ASTM D5191-96). It is recognised that the lower the RVP value, the lower the emissions from such compositions.

It is a legal requirement in some countries, e.g. the USA, that fuels incorporate oxygen in the fuel, which oxygen may be present in the form of an organic oxygen containing compound. Ethanol is one such compound. However, according to the SAE publication "Automotive Fuels", Edited by Keith Owen and Trevor Coley, published by SAE (1995), Chapter 11, ethanol actually increases dramatically the RVP of a gasoline composition containing the same. Thus, it would have been expected that in addition to increasing evaporative emissions, presence of ethanol would also lead to driveability and operability problems. Surprisingly, it has now been found that the fuel compositions of the present invention may further benefit by adding ethanol thereto and reduces emissions due, e.g., to running losses and dirunal losses.

The amount of ethanol used for this purpose is greater than 0.5% by volume, suitably greater than 1.0 % by volume and is preferably in the range from 1.5 to 10.0 % by volume, more preferably from 5 to 10% by volume of the total fuel composition. In this manner the RVP debit associated with ethanol addition can be reduced.

Thus according to a further embodiment, the present invention is a fuel composition comprising gasoline having a sulphur content of less than 10 ppm by weight and an aromatic content of less than 25% by volume, characterized in that said composition comprises at least 5% by volume of olefins, greater than 0.5% by volume of ethanol and is substantially free of any ethers.

A feature of the invention is the ability of the olefins to reduce the reported adverse effects of ethanol on the RVP of gasoline compositions. This ability of the olefins had not been recognised hitherto. Thus, the RVP debit associated with ethanol addition can be reduced by at least 0.69 kPa (0.1 psi) by using a gasoline composition according to the present invention. This reduction may appear insignificant in absolute terms but in terms of overall evaporative losses of fuel, it is a substantial reduction. Since the tendency of current environmental legislation throughout the world is to progressively reduce sulphur and aromatics content of fuels and also to minimise RVP at the same time ensuring that the composition has adequate volatility for efficient combustion, the benefits to the industry are all too apparent.

The fuel compositions of the present invention can be prepared by blending the various components into a base fuel. All of the olefins and aromatics can be blended as part of the refining process during the preparation of the fuel itself since these are readily soluble and miscible with the base fuel. The blending of ethanol may have to be carried out at the point of distribution, in spite of its solubility in the base fuel, to comply with requirements in

certain countries which disapprove of such compositions containing ethanol being transported via pipelines.

Thus, the present invention provides a fuel with relatively good lubricity and high
5 octane performance while attaining low vehicle emissions.

The present invention is further illustrated with reference to the following Examples. The ultra-low sulphur motor gasoline used in the Examples was prepared from a blend of refinery streams. Into this gasoline was blended a mixture of olefinic hydrocarbons prepared
10 from commercial chemicals to mimic those found in gasoline. The resulting gasoline-olefin blends were analysed by FIA to measure the levels of olefins and aromatics therein and the performance of these blends was evaluated using the HFRR technique described below under the standard motor gasoline conditions. As a comparison base fuels with higher levels of sulphur were also tested. The various analyses and performance results are tabulated
15 below:

The antiwear and lubricity performance of the fuel compositions of the present invention were measured according to the so-called high frequency reciprocating rig test (hereafter referred to as "HFRR"). The HFRR test consists of a loaded upper ball 6mm in
20 diameter, which oscillates against a static lower plate. Both friction and contact resistance are monitored throughout the test. The tests are conducted largely according to the standard procedure published as CEC F-06-A-96 in which a load of 2N (200g) was applied, the stroke length was 1mm, the reciprocating frequency was 50 Hz and sample temperature of 25°C. The ambient temperature and humidity were controlled within the
25 specified limits and the calculated value of wear scar diameter was corrected to the standardized water vapour pressure of 1.4 kPa. The specimen ball was a grade 28 (ANSIB3.12), AISI E-52100 steel with a Rockwell hardness "C" scale (HRC) number of 58-66 (ISO 6508), and a surface finish of less than 0.05 μ m R_a, and the lower plate was AISI E-52000 steel machined from annealed rod, with a Vickers hardness "HV30" scale number of
30 190-210 (ISO 6507/1). It is turned, lapped and polished to a surface finish of 0.02 μ m R_a.

TABLE 1: Summary of HFRR test conditions

Fluid volume, ml	3.6 ± 0.20	Specimen steel	AISI E-52100
Fluid temperature, °C	25	Ball diameter, mm	6.00
Bath surface area, cm ²	6.0 ± 1.0	Surface finish (ball)	< 0.05 µm Ra
Stroke length, mm	1.0 ± 0.02	Hardness (ball)	58 - 66 Rockwell C
Frequency, Hz	50 ± 1	Surface finish (plate)	< 0.02 µm Ra
Applied load, g	200 ± 1	Hardness (plate)	190 - 210 HV 30
Test duration, minutes	75 ± 0.1	Ambient conditions	See text

TABLE 2: FIA ANALYSIS

5

Components	1	2	3	4	5	6
Aromatics	22	22	21	21	44.7	38.7
Olefins	0.6	4.8	8.5	9.4	2.3	6.2
Sulphur*	9	-	-	-	51	180

* measured by UV fluorescence (ASTM D5453-93)

TABLE 3: HFRR TEST RESULTS

Parameters	1	2	3	4	5	6
Olefin content (%)	0.5	5.0	8.5	9.5	2.3	6.2
Friction	0.513	0.482	0.459	0.428	-	-
Wear Scar (µm)	912	909	883	826	862	827

10

TABLE 4: HFRR WEAR-SCAR (µm) OF MOTOR GASOLINE WITH INCREASING OLEFIN AND SULPHUR CONTENT

Olefins (wt %)	Sulphur Content (ppm)		
	< 10	50	180
0.5	912	862	827
5.0	909		
8.5	883		
9.5	826		

The above results show that by reducing the sulphur content and aromatic content has an adverse effect on lubricity. They also show that this deterioration can be reversed by increasing the olefin content of the fuel.

5 In respect of RVP testing base fuel A was prepared according to the composition shown in Table 5 below where the values (%) are by volume.

Table 5

Fuel	Sulphur (ppm)	RVP (kPa)	Olefins (%)	Aromatics (%)	Saturates (%)
A	9	52.1	0.3	22	77.5

10

The RVP test results are shown in Table 6 below:

TABLE 6

Add Hydrocarbon vol %	RVP kPa	Add EtOH vol %	RVP kPa	EtOH Effect kPa	Avg. Effect
Base Fuel A	52.1	5	58.6	6.5	
5 Saturates	50.6	5	58.3	7.7	
10 Saturates	50.4	5	58.5	8.1	7.9
15 Saturates	50.6	5	58.4	7.8	
5 Olefins	51.2	5	58.7	7.5	
10 Olefins	52.2	5	59.2	7.0	7.3
15 Olefins	53.0	5	60.4	7.4	
5 Aromatics	48.3	5	55.9	7.6	
10 Aromatics	46.3	5	53.9	7.6	7.6
15 Aromatics	44.3	5	52.0	7.7	

15

Claims:

1. A fuel composition comprising gasoline having a sulphur content of less than 10 ppm by weight and an aromatic content of less than 25% by volume, characterized in that said composition comprises at least 5% by volume of olefins and is substantially free of any ethers.

5 2. A fuel composition according to Claim 1 wherein the sulphur content of the fuel composition is less than 5 ppm by weight.

10 3. A fuel composition according to Claim 1 or 2 wherein the aromatic content of the composition is less than 20% by volume.

15 4. A fuel composition according to any one of the preceding Claims wherein the fuel composition comprises at least 10% by volume of olefins based on the total volume of the composition.

20 5. A fuel composition according to any one of the preceding Claims wherein the fuel composition comprises from 10-25% by volume of olefins based on the total volume of the composition.

6. A fuel composition according to any one of the preceding Claims wherein the olefin present in said composition comprises one or more of C₃-C₁₀ olefins.

25 7. A fuel composition according to any one of the preceding Claims wherein the olefin present in said composition is selected from one or more of pent-1-ene, hex-1-ene, hept-1-ene, oct-1-ene, non-1-ene and dec-1-ene.

30 8. A fuel composition of reduced RVP comprising gasoline having a sulphur content of less than 10 ppm by weight and an aromatic content of less than 25% by volume, characterized in that said composition comprises at least 5% by volume of olefins, greater than 0.5% by volume of ethanol and is substantially free of any ethers.

35 9. A fuel composition according to Claim 8 wherein the amount of ethanol present in said composition is in the range from 1.5 to 10.0 % by weight of the total fuel composition.

10. A fuel composition according to Claim 8 or 9 wherein said composition has an RVP value below 62 kPa (9 p.s.i.).

INTERNATIONAL SEARCH REPORT

Inte *ional Application No

PC1/EP 01/02620

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C10L1/06

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 7 C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US H1305 H (TOWNSEND DANIEL J ET AL) 3 May 1994 (1994-05-03) claims 13,14,20,23 column 3, line 43 - line 54 ---	1,3,8-10
A	EP 0 596 611 A (NIPPON OIL CO LTD) 11 May 1994 (1994-05-11) claims 1-3 tables 2-4 ---	1,2,6,7
A	US 5 837 126 A (JESSUP PETER J ET AL) 17 November 1998 (1998-11-17) claim 1 column 4, line 57 - line 63 column 18, line 7 - line 9 tables 2,5 ---	1,3-5,8, 10 -/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° 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 document 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 24 July 2001	Date of mailing of the international search report 02/08/2001
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer De Herdt, O

INTERNATIONAL SEARCH REPORT

International Application No
PC1/EP 01/02620

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 653 866 A (JESSUP PETER J ET AL) 5 August 1997 (1997-08-05) claim 1 column 4, line 57 - line 63 tables 2,5 ---	1, 3-5, 8, 10
A	EP 0 292 298 A (NIPPON OIL CO LTD) 23 November 1988 (1988-11-23) claim 1 ---	1
P, A	US 6 039 772 A (ORR WILLIAM C) 21 March 2000 (2000-03-21) claims 1,3,4,6,8 column 15; table I column 16, line 51 -column 17, line 17 ---	1, 4, 5, 8-10
P, A	US 6 132 479 A (WELSTAND JOSEPH S ET AL) 17 October 2000 (2000-10-17) claims 1,2 ---	1
A	US 5 346 609 A (FLETCHER DAVID L ET AL) 13 September 1994 (1994-09-13) claim 1 tables 3,4 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 01/02620

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US H1305	H	03-05-1994	NONE		
EP 0596611	A	11-05-1994	JP 6128570 A	10-05-1994	
			DE 69319302 D	30-07-1998	
			DE 69319302 T	29-10-1998	
			US 5401280 A	28-03-1995	
US 5837126	A	17-11-1998	US 5653866 A	05-08-1997	
			US 5593567 A	14-01-1997	
			US 5288393 A	22-02-1994	
			US 6030521 A	29-02-2000	
US 5653866	A	05-08-1997	US 5593567 A	14-01-1997	
			US 5288393 A	22-02-1994	
			US 6030521 A	29-02-2000	
			US 5837126 A	17-11-1998	
EP 0292298	A	23-11-1988	JP 3075598 B	02-12-1991	
			JP 63289094 A	25-11-1988	
			JP 3075595 B	02-12-1991	
			JP 63317590 A	26-12-1988	
			AU 595450 B	29-03-1990	
			AU 1647188 A	24-11-1988	
			CA 1306356 A	18-08-1992	
			DE 3863972 A	05-09-1991	
			KR 9606006 B	06-05-1996	
			US 4824552 A	25-04-1989	
US 6039772	A	21-03-2000	AT 69462 T	15-11-1991	
			AU 6377586 A	24-03-1987	
			CA 1310832 A	01-12-1992	
			DE 3682503 A	19-12-1991	
			DE 3682503 D	19-12-1991	
			EP 0235280 A	09-09-1987	
			WO 8701384 A	12-03-1987	
US 6132479	A	17-10-2000	NONE		
US 5346609	A	13-09-1994	AU 661863 B	10-08-1995	
			AU 2465292 A	16-03-1993	
			CA 2113810 A	16-02-1993	
			DE 69223809 D	05-02-1998	
			DE 69223809 T	23-04-1998	
			EP 0641375 A	08-03-1995	
			JP 2788348 B	20-08-1998	
			JP 6509830 T	02-11-1994	
			US 5318690 A	07-06-1994	
			US 5360532 A	01-11-1994	
			US 5391288 A	21-02-1995	
			WO 9304146 A	04-03-1993	
			US 5411658 A	02-05-1995	
			US 5401389 A	28-03-1995	
			US 5500108 A	19-03-1996	
			US 5510016 A	23-04-1996	
			US 5503734 A	02-04-1996	
			US 5643441 A	01-07-1997	
			US 5409596 A	25-04-1995	
			US 5348641 A	20-09-1994	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 01/02620

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US 5346609	A	US	5413696 A	09-05-1995
		US	5352354 A	04-10-1994
		US	5407559 A	18-04-1995
		US	5413697 A	09-05-1995
		US	5308471 A	03-05-1994
		US	5413698 A	09-05-1995
		US	5290427 A	01-03-1994
		US	5362376 A	08-11-1994
		US	5326462 A	05-07-1994
		US	5298150 A	29-03-1994
		US	5320742 A	14-06-1994
		US	5326463 A	05-07-1994
		US	5399258 A	21-03-1995