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(54) Title: HYDROCARBON FUEL COMPOSITION CONTAINING AN ESTER

(57) Abstract: This invention relates to the use of esters with low water solubility as oxygenates in gasoline fuels. This invention relates to a gasoline fuel, comprising an ester and butane, wherein the ester contains 5 to 14 carbon atoms. This invention also relates to using a low water solubility ester as an oxygenate in automotive gasoline used in internal combustion engines. Additionally, the invention provides a gasoline fuel, comprising an ester, wherein the ester has a water solubility of less than about 15,000 mg/L at 20 °C, preferably less than about 6,500 mg/L at 20 °C and the fuel has an overall water solubility of less than about 5,000 mg/L at 20 °C.



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Hydrocarbon Fuel Composition Containing an Ester

This invention relates to the use of esters with low water solubility as oxygenates in gasoline fuels.

5 The Clean Air Act Amendments of 1990 (CAA90) mandated the use of cleaner burning hydrocarbon fuels. Under the CAA90, approximately 40 urban areas throughout the United States were required to use oxygenated fuels during the winter months to meet ambient CO standards beginning in 1992. These fuels are referred to as "winter
10 oxygenated fuels" or "oxy-gasoline" and they must contain a minimum of 2.7 weight percent oxygen. A second requirement under the CAA90 requires "reformulated gasoline" ("RFG") to be used in the nine cities with ozone levels classified as "severe" or "extreme" beginning in 1995. RFG must contain a minimum of 2.0 weight percent oxygen. California also
15 instituted a statewide winter oxygenate program in 1992. Additionally, after March 1, 1996, all gasoline sold in California is required to be Phase II reformulated gasoline referred to as California Air Resources Board (CARB) Phase II gasoline. CARB Phase II gasoline contains stricter gasoline formulation provisions than the Federal RFG program and
20 mandates 1.8 to 2.2 wt.% oxygen content in gasoline.

Most gasoline suppliers meet the oxygenate requirements of the different clean fuels programs by adding Methyl Tertiary Butyl Ether (MTBE) to gasoline blend stocks. MTBE is the oxygenate used in 84% of RFG, which accounts for 32% of all gasoline sold in the United States
25 according to *Sissell*, Chemical Week, Volume 160, No. 15, p. 41 (April 22, 1998).

The 2.7 wt.% oxygen requirement of winter oxy-gasoline requires the addition of approximately 15 volume percent of MTBE, while the 2.0 wt.% oxygen requirement of RFG requires the addition of approximately
30 11 volume percent of MTBE. To a much lesser extent ethanol (EtOH),

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ethyl-tert butyl ether (ETBE), tert-amyl methyl ether (TAME), and tertiary-butyl alcohol (TBA) are used or have been suggested as oxygenates in gasoline. The oxygenates listed above are currently approved oxygenates for inclusion in gasoline.

5 Recently, various environmental protection agencies have begun raising concerns regarding the detection of MTBE in surface and ground water. In one study conducted by the Lawrence Livermore National Laboratory, 236 leaking underground fuel tank (LUFT) sites in California were evaluated. In 1995 and 1996, 78% of these LUFT sites reported
10 detection of MTBE in ground water. Happel, *An Evaluation of MTBE Impacts to California Groundwater Resources*, Lawrence Livermore National Laboratory (June 11, 1998). The maximum concentration of MTBE found by the Livermore Study sites ranged from several mg/L to approximately 100,000 mg/L. *Happel*, June 11, 1998.

15 The following results demonstrate the extent to which MTBE dissolves in water from a motor gasoline blend. The data also demonstrates that the dissolved concentration of MTBE increases as the concentration of MTBE in gasoline increases.

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MAXIMUM SOLUBILITY OF MTBE &
BENZENE IN GROUND WATER
Laboratory Equilibrium Results
(Water: Gasoline Ratio of 10:1)

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<u>% in Gasoline</u>	<u>MTBE (ppm)</u>	<u>Benzene (ppm)</u>
0% MTBE	0	65
5% MTBE	1755	60
10% MTBE	3650	60
15% MTBE	5142	57
10% TAME	1259	59

B. Bauman, MTBE and Groundwater Quality: Bioremediation Research,
EPA OUST National Conference (March 12, 1997)

One reason for MTBE's prevalence in ground water is MTBE's high
10 solubility in water. Similarly, all of the oxygenates currently used in
gasoline have a relatively high water solubility as compared to
conventional gasoline hydrocarbon compounds which do not contain
oxygen. A summary of some of these oxygenates' solubility in water is
reported in Zogorski et al., *Fuel Oxygenates and Water Quality*, which is
15 annotated below to include other oxygenates:

<u>Property</u>	<u>MeOH</u>	<u>EtOH</u>	<u>TBA</u>	<u>MTBE</u>	<u>ETBE</u>	<u>TAME</u>	<u>TBAc*</u>	<u>MP**</u>	<u>MiB</u>	<u>DIPE</u>	<u>TBF</u>
Water Solubility (mg/L)	Infinite	Infinite	Infinite	43,000- 54,300	~26,000	~20,000	9,000	5,600 @20°C	~14,000	9,000 @20°C	~40,000

Values are at 25°C unless otherwise indicated. TBF = tertiary-butyl formate, TBAc = tert-Butyl Actate, MP - methyl pivalate, MiB = methyl isobutyrate.

* Lyondell Chemical Worldwide, Inc. Material Safety Data Sheet (7 Dec 1998)

** Exxon Chemicals Americas Material Safety Data Sheet (8 Nov 1989)

20 The above table displays the solubility of some oxygenated
compounds in water as reported in one reference with some annotations.
A higher number in mg/L for a particular compound corresponds to a
higher water solubility for that compound. The listed alcohols have the
highest water solubilities, indicated by the term infinite, and are completely
25 miscible with water. Methyl pivalate has the lowest solubility in water at
5,600 mg/L at 20°C.

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Hydrocarbon water contamination can occur when a fuel comes into contact with a surface or subsurface body of water. Potential sources of such contamination could include emissions or spills of an oxygenate, non-oxygenated or oxygenated liquid fuel during the production of the fuel including, for example, refining or blending of the fuel. A second potential source includes spills or emissions occurring while the oxygenate, non-oxygenated or oxygenated fuel is stored in above-ground or underground storage tanks. Refineries and gasoline bulk plants commonly store fuels and fuel blend stocks in above-ground, fixed-roof or floating roof storage tanks. Fuel distribution facilities including, for example fuel bulk plants and gasoline service stations, commonly store fuels in carbon steel or fiberglass underground storage tanks. A third potential source includes spills or emissions occurring while the oxygenate or oxygenated fuel is transported by pipeline, tanker truck or rail car. A fourth potential source includes spills or emissions occurring while the fuel is dispensed into fuel-powered vehicles from distribution points like gasoline service stations. A fifth potential source is the use of oxygenated fuels in boating and recreational vehicles on lakes, rivers and other waterways. Many of the above-described sources of potential water contamination are also sources of potential air emissions through volatilization of liquid fuels. Additionally, it is theorized that MTBE can be volatilized and later dissolved in rain water, which is subsequently transported to surface or subsurface water.

Motor gasoline also contains various volatile organic compounds (VOC's), some of which may be involved in complex photochemical atmospheric reactions, along with oxygen and nitrogen oxides (NO_x) in the atmosphere under the influence of sunlight, to produce ozone. Ozone formation is a problem in the troposphere (low atmospheric or "ground-based"), particularly in an urban environment, since it leads to the phenomenon of smog. Since VOC emissions are a source of ozone

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formation, motor gasoline manufacture and formulation are regulated to attain ozone compliance. Historically, governmental regulation of motor gasoline has focused on limiting the volatility of motor gasoline sold in the United States. Currently, motor gasoline volatility is regulated through
5 seasonally limiting motor gasoline Reid Vapor Pressure (“RVP”). A listing of EPA’s regulatory motor gasoline RVP limits is found at 40 C.F.R. 80.27, *Controls and Prohibitions on Gasoline Volatility*, the entirety of which is hereby incorporated by reference.

The United States Environmental Protection Agency (EPA) has
10 developed National Ambient Air Quality Standards (NAAQS) for six pollutants: ozone, nitrogen oxides (NO_x), lead, carbon monoxide, sulfur dioxide and particulates. Ground-level ozone, a primary component of smog, exceeds target levels in many areas of the United States. The CAA90, for example, includes provisions to reduce urban ozone levels.
15 Reformulated gasoline is targeted to reduce ozone forming hydrocarbon emissions in the United States worst ozone non-attainment areas by 15 percent in 1995 and by 20 percent by 2000. The CAA90 includes several programs to reduce urban ozone including stricter automobile tailpipe emissions limits of 0.25 grams per mile non-methane hydrocarbons and
20 stricter gasoline RVP limits. Therefore, ozone non-attainment has an impact on motor gasoline formulation through regulatory seasonal RVP limitations and gasoline reformulation.

According to current VOC emission regulations in the U.S.A., organic compounds, including some gasoline components belong to one
25 of two groups depending on their reactivity toward atmospheric photochemical ozone formation:

- (a) Negligible reactivity organic compounds which generate about the same or less quantity of ozone as would be produced by the same weight % as ethane. These organic
30 compounds are exempt from the definition of a VOC and are

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not considered to be a VOC in any fluid composition. There are numerous such compounds exempted by the EPA from the definition of VOC. Other such organic compounds, such as tertiary-butyl acetate, which is under exemption consideration by the EPA, may be too chemically and thermally unstable for motor gasoline applications.

(b) Currently, other oxygenated and hydrocarbon compounds are considered to be VOC's and treated by the EPA as equally (on a weight basis) polluting. However, it would be useful to differentiate organic compounds on the basis of their ability to generate ozone. Thereby, regulating a particular hydrocarbon compound based on its potency to form ozone in relationship to other hydrocarbon compounds.

Recently California's Governor banned the use of MTBE in gasoline sold in California after December 31, 2002. See *Sissell*, Chemical Week, Volume 161, No. 13, p. 7 (April 7, 1999). Regulatory and industry representatives are currently evaluating the possibility of meeting California's gasoline oxygenate requirements through the use of alcohols. It would be desirable if esters with low water solubility could be used to meet the oxygenate requirement of RFG, Carb Phase II gasoline and oxy-gasoline fuels. These low solubility esters would have a reduced solubility in surface and subsurface water and could therefore reduce the impact on such waters from spills and emissions of oxygenated fuels. It would also be desirable for MTBE replacements, including these esters, to have other favorable properties such as low ozone formation potential and a low rubber seal swelling tendency.

This invention relates to a gasoline fuel, comprising an ester and butane, wherein the ester contains 5 to 14 carbon atoms. This invention also relates to using a low water solubility ester as an oxygenate in

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automotive gasoline used in internal combustion engines. Additionally, the invention provides a gasoline fuel, comprising an ester, wherein the ester has a water solubility of less than about 15,000 mg/L at 20°C, preferably less than about 6,500 mg/L at 20°C and the fuel has an overall
5 water solubility of less than about 5,000 mg/L at 20°C.

Another embodiment provides a method for aiding in reducing subsurface and surface water contamination caused at least in part by production, distribution, storage and/or use of oxygenated fuels. The embodiment provides a method for reducing subsurface and surface
10 water contamination. The method comprises producing a gasoline fuel containing an ester for use in spark-ignition engines, wherein the ester has a water solubility of less than about 15,000 mg/L at 20°C, preferably less than about 6,500 mg/L at 20°C, thereby reducing subsurface and surface water contamination caused at least in part by production, distribution,
15 storage and/or combustion of oxygenated fuels as compared to oxygenated fuels containing oxygenates with a water solubility greater than about 15,000 mg/L at 20°C.

The invention also includes a method of producing lower cost oxygenated gasoline fuels. The method includes making fuels compliant
20 with the applicable maximum regulatory RVP limit for the fuel. The method comprises:

- (a) adding an ester to a gasoline blend stock, wherein the ester contains 5 to 14 carbon atoms and has a RVP less than about 4 pounds per square inch; and
- 25 (b) adding at least one lower cost gasoline blending component selected from butane, isobutane, and isopentane to said gasoline blend stock, wherein said lower cost gasoline blending component has a RVP of greater than the maximum regulatory RVP limit for said gasoline fuel, such

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that the blended gasoline meets regulatory RVP requirements.

This compositional opportunity is created by the low RVP of the esters according to the invention, thereby enabling additional high RVP,
5 high octane, and low cost paraffins (butanes and isopentane) to be incorporated at an increased concentration.

The invention also includes a method for reducing atmospheric ozone formation. The method comprises producing a gasoline fuel containing an ester for use in spark-ignition engines, wherein the ester has
10 a RVP of less than about 4 pounds per square inch. The method reduces atmospheric ozone formation caused at least in part by production, distribution, storage and/or combustion of preferred oxygenated fuels as compared to oxygenated fuels containing oxygenates with a RVP of greater than about 4 pounds per square inch.

15 The invention includes a second method of reducing atmospheric ozone formation. The method comprising producing a gasoline fuel containing an ester for use in spark-ignition engines, wherein the ester has an absolute MIR, as defined herein, of less than about 1.5 gram ozone/gram ester, thereby reducing atmospheric ozone formation caused
20 at least in part by production, distribution, storage and/or combustion of oxygenated fuels as compared to oxygenated fuels containing oxygenates having an Absolute MIR of greater than about 1.5 gram ozone/gram ester. Additionally, the preferred oxygenated compositions of the instant invention are products whose absolute maximum incremental reactivity
25 (absolute MIR) is below 1.5g ozone/gram of compound (low), preferably below 1.0g ozone/gram of compound (very low) or most preferably below 0.5g ozone/gram compound (negligible).

The invention also includes a method for reducing the deterioration of rubber seal and other rubber components in the fuel distribution system
30 in fuel powered engines that combust oxygenated gasoline fuels. The

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method comprises producing a gasoline fuel containing an ester for use in the fuel-powered engines, wherein the ester has a total Hansen solubility parameter of less than about 8.5 calorie^{1/2} per centimeter^{3/2}, thereby reducing rubber-seal deterioration in said fuel-powered engines as compared to oxygenated fuels containing oxygenates with a Hansen solubility parameter of greater than about 8.5 calorie^{1/2} per centimeter^{3/2}. The unit "calorie^{1/2} per centimeter^{3/2}" represents the common form of Hansen solubility used in the United States and is represented as "[cal^{1/2}/cm^{3/2}]" throughout this application.

Yet another embodiment of this invention is to provide oxygenated fuels containing esters wherein the claimed esters are advantaged versus esters of linear acids in terms of rates of hydrolysis and advantaged in terms of rates of chemical and thermal decomposition versus tert-butyl acetate. Tert-butyl acetate thermally decomposes to isobutylene and acetic acid. Acetic acid and other carboxylic acids contribute to deposit (sludge) formation and are to be avoided in spark engine systems.

These embodiments and additional features of the invention will become apparent from the following detailed description and appended claims.

As used herein and in the claims, the term "oxygenate" refers to all organic compounds that contain the element oxygen. Oxygenates include, but are not limited to, methyl tertiary-butyl ether (MTBE), ethanol (EtOH), ethyl-tert butyl ether (ETBE), tert-amyl methyl ether (TAME), and tertiary-butyl alcohol (TBA).

As used herein and in the claims, the terms "gasoline", "gasoline fuel" and "liquid gasoline fuel" refer to any combustible liquid composition containing a substantial proportion of gasoline boiling range organic compounds (i.e., butane to about 477°F). Gasoline fuels include, but are not limited to, motor gasoline and aviation fuel.

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As used herein and in the claims, the terms “motor gasoline” and “automobile gasoline” include all gasoline formulations used in internal combustion vehicles. Motor gasoline includes, but is not limited to, conventional gasoline, reformulated gasoline, oxy-gasoline and CARB
5 Phase I & II gasoline.

As used herein and in the claims, the term “fuel-powered vehicle” includes any vehicle that utilizes a liquid hydrocarbon fuel as a source of power to propel, directly or indirectly, the vehicle. Fuel-powered vehicles include vehicles that combust gasoline in internal combustion engines as
10 a source of power to propel the vehicle. Combustion of a gasoline fuel in an internal combustion engine also includes those engines that atomize the gasoline fuel prior to combustion. Fuel powered vehicles, include, but are not limited to, gasoline-powered automobiles, gasoline-powered boats and ships, and airplanes that combust aviation gasoline.

15 As used herein and in the claims, the term “distribution point” refers to a facility that stores and distributes gasoline fuels to users of such fuels. Such facilities include, but are not limited to, gasoline service stations, fuel bulk plants and private fuel distribution facilities.

It is well known in the art that ethers are used as motor gasoline
20 additives to enhance the quality of the motor gasoline due to environmental regulations, both existing and pending, in the United States. By using an oxygenate rather than its counterpart olefin in motor gasoline, less carbon monoxide is produced upon combustion of the motor gasoline. Also, the rules regulating reformulated gasoline and other clean fuels
25 require a lower olefin content in gasoline due to olefins tendency to contribute to ozone formation more than their counterpart ethers.

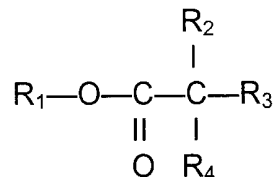
A potential advantage of using an ester rather than an ether in motor gasoline is that the ester also has a lower RVP. The inclusion in the gasoline of ester components having low RVP enables the concurrent
30 inclusion of high RVP paraffins such as butane, isobutane and

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isopentane, so as to meet the overall RVP requirements of the fuel. Regulatory RVP requirements are tailored for seasonal and geographical variations and provide sufficient fuel volatility for engine start-up among other attributes.

5 The esters of the invention contain 5 to 14 carbon atoms. Many of the esters, according to the invention, are generally of a higher carbon number than most oxygenates currently available as gasoline oxygenates. In one embodiment, the esters of the invention include esters with solubility in water of less than about 15,000 mg/L at 20°C, preferably less
10 than about 6,500 mg/L at 20°C. Preferably, the esters contain at least one branched alkyl group. A greater amount and degree of branching generally provides esters with greater octane number. Molecules with greater research and motor octane are favored. Preferably, the esters have the following formula:

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wherein R₁ is selected from the group consisting of alkyl groups containing one to ten carbon atoms, and wherein R₂, R₃ and R₄ contain a total of 2 to 11 carbon atoms, where either R₂ or R₃ or R₄ can be hydrogen.
25 Preferably, R₁ is selected from the group consisting of methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, neopentyl and 3,5,5-trimethyl hexyl; R₂ is selected from the group consisting of hydrogen, methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl and neopentyl; R₃ is selected from the group consisting of
30 hydrogen, methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-pentyl, isopentyl and neopentyl; and R₄ is selected from the group consisting of hydrogen, methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl,

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sec-butyl, tert-butyl, n-pentyl, isopentyl and neopentyl. Preferably, only one of R_2 , R_3 and R_4 can be hydrogen. Preferably R_2 , R_3 and R_4 each have at least one carbon atom, more preferably R_2 , R_3 and R_4 contain a total of 3 to 7 carbon atoms and, most preferably, are esters of pivalic acid
5 ($R_1 = R_2 = R_3 = CH_3$).

In one embodiment, the esters used in the invention have a solubility in water of less than about 15,000 mg/L at 20°C, preferably of less than about 6,500 mg/L at 20°C. More preferably, they have solubility in water of less than about 5,000 mg/L at 20°C. Even more preferably,
10 they have solubility in water of less than about 3,000 mg/L at 20°C. Most preferably, they have water solubility of less than about 1,000 mg/L at 20°C. Solubility in water is important in determining the concentration of a compound that dissolves into the water phase from a hydrocarbon mixture in contact with water. Generally, low solubility in water favors lower water
15 phase partitioning from the hydrocarbon phase into the water phase. Therefore, oxygenates with lower water solubility used in gasoline fuels are expected to have a lower concentration in the water phase upon contact of the gasoline fuel with water.

The esters used in the present invention can be blended into a
20 variety of liquid fuels. The fuels of the invention are generally gasoline fuels, especially motor gasoline. The gasoline fuels of the invention include both leaded and unleaded gasoline. Preferably, the gasoline fuels of the invention are unleaded gasolines. These fuels are, for example, derived from refining crude oil and blending various refinery process
25 streams to meet various motor gasoline performance and regulatory guidelines. Refinery process streams used as gasoline blend stocks according to the invention may include, but are not limited to, butanes, straight run gasoline, sulfuric and hydrofluoric acid alkylation alkylate, fluidized catalytic cracker gasoline, platinum reformer reformat,
30 hydrotreated coker olefins, aromatics and raffinate. Generally, the motor

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gasoline components, according to the invention, are those hydrocarbon compounds in the motor gasoline boiling range (i.e., butane through about 437°F).

5 The invention also includes preparing gasoline blend stocks that include the esters of the invention. These blend stocks are normally used as constituents of finished motor gasoline although the blend stocks may not meet all of the performance and/or regulatory guidelines of a particular fuel.

10 In one embodiment, the fuels, according to the invention, include butane, and other high octane, high vapor pressure hydrocarbons. In particular, butane, isobutane and isopentane may be used as low cost blending components. However, in current oxygenated gasolines, the use of these components is limited by the overall regulatory fuel RVP specifications. This is because the high RVP of such oxygenates as
15 ethanol and MTBE leaves very little room for addition of these high-quality, low-cost paraffinic components.

Many of the esters, according to the invention, and butane are high octane number blending components. The esters, according to the invention, may optionally be used in combination with butane to formulate
20 a gasoline blend that contains a reduced amount of straight chain (normal) paraffins. Higher carbon number normal paraffins, for example pentane, hexane, heptane and octane, are low octane number gasoline components. Some of these normal paraffins, for example pentane and hexane, are also high RVP gasoline components.

25 The gasoline fuels comprising an ester according to the invention have an overall solubility in water less than about 7,000 mg/L at 20°C. Preferably the fuels have a water solubility of less than about 5,000, 3,000, 2,000 or 1,500 mg/L at 20°C. More preferably the fuels of the invention have a water solubility of less than about 1,200 mg/L at 20°C or
30 1,000 mg/L at 20°C. Most preferably, the fuels of the invention have a

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water solubility of less than about 800, 700, 500, 300, 200, or 150 mg/L at 20°C. Esters of the instant invention can be used in fuels containing other oxygenates. Preferably the fuels of the invention contain less than about 2.0, 1.0 or 0.5 volume percent of other oxygenated components and most preferably about 0.0 volume percent of other oxygenated components. The fuels of the invention may contain less than about 2.0, 1.0 or 0.5 volume percent of MTBE and most preferably about 0.0 volume percent of MTBE.

Many of the esters, according to the invention, contain a significantly higher oxygen content than the oxygenates currently used in motor gasoline. Generally, esters have two times greater oxygen content per mole as compared to ethers. Therefore as compared to a gasoline blend containing ethers, an ester oxygenated gasoline formulation would need only one half the moles of ester to meet a regulatory oxygen requirement. For example, methyl pivalate ("MP") contains about 27.6 weight percent of oxygen as compared to MTBE, which contains about 18.2-weight percent oxygen. Therefore, less volume of MP is required in order to obtain a certain weight percent of oxygen in motor gasoline. For example, in order to obtain the 2.0 wt.% oxygen requirement of RFG a motor gasoline blender must add approximately 11 volume percent of MTBE. The same oxygen requirement can be obtained with only about 7.25 volume percent of MP.

The esters according to the invention can be used to meet the various clean fuel programs oxygenate requirements. For example, the 2.7 wt.% oxygen requirement of winter oxy-gasoline, the 2.0 wt.% oxygen requirement of RFG or the 1.8 to 2.2 wt.% oxygen content requirement of CARB Phase II gasoline, can be met by the addition of the esters according to the invention. Preferably, the ester provides greater than about 1.0 weight percent of oxygen to the fuel. Preferably, the ester provides greater than about 1.5 or 1.8 weight percent of oxygen to the

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fuel. Preferably, the ester provides greater than about 2.0 or 3.0 weight percent oxygen to the fuel. Due to their low or very low RVP, the esters in the instant invention can be used in fuels at even higher oxygen content, providing additional improvement in the combustion properties of the fuel.

5 The esters of the invention may be used to produce cleaner burning fuels upon combustion in fuel powered engines. Current EPA clean fuels' regulations place limits on certain motor gasoline components and properties. For example, 40 C.F.R. 80.41, *Standards and Requirements for Compliance*, places limitations on motor gasoline RVP, benzene and
10 oxygen content. The regulations also specify target reductions of volatile organic compound emissions, toxic air pollutant emissions, and nitrogen oxide emissions. The emission reductions are calculated through different predictive models used to calculate motor gasoline blend emissions based on various fuel parameters, including the benzene content, sulfur content,
15 olefin content, oxygen content, and RVP of the fuel. See 40 C.F.R. 80.42-43.

One such standard places a per gallon and average limitation on motor gasoline benzene content. The fuels of the invention may also provide a low benzene content fuel. The fuels of the invention may
20 optionally contain less than about 2.0 volume percent benzene. Preferably, less than about 1.5 volume percent benzene. More preferably, less than about 1.0, 0.8 or 0.5 volume percent benzene.

Aromatic compounds are a major component of gasoline, generally providing needed octane. The esters of this invention may be used as a
25 partial replacement of aromatic compounds. Moreover, the fuels of the invention can optionally include low aromatic content fuels. The fuels of the invention may optionally contain less than about 30.0 volume percent of aromatic compounds. Preferably, less than about 25.0 volume percent aromatics. More preferably, less than about 20.0, 15.0 or 10.0 volume
30 percent aromatics.

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The fuels of the invention may optionally contain less than about 20.0 volume percent of olefinic compounds. Preferably, less than about 15.0 volume percent olefins. More preferably, less than about 10.0, 5.0 or 2.0 volume percent olefins. Most preferably, the fuels contain about 0.0
5 volume percent olefins. The fuels of the invention may optionally contain less than about 400.0 ppm sulfur. Preferably, less than about 350.0 ppm sulfur. More preferably, less than about 300.0, 250.0, 200.0, 150.0 or 100.0 ppm sulfur. Most preferably, the fuels contain less than about 50.0, 30.0 or 10.0 ppm sulfur.

10 The invention may also provide a method of producing lower cost oxygenated gasoline fuels. The method takes advantage of the anticipated lower RVP of the higher carbon number esters used in this invention. When a starting motor gasoline feedstock has a high RVP level, one could be limited on how much MTBE or TAME addition is
15 possible to achieve the required octane requirements, while at the same time, not exceeding the RVP limit. Therefore, an additional embodiment of the present invention includes the use of one or more esters of the invention to achieve the maximum octane boosting effect and without the corresponding undesirable increase in RVP. Many of the prior art
20 oxygenates have relatively high vapor pressures. For example, MTBE has a blending RVP of 57.9 kPa (8.4 psi) and TAME has a blending RVP of 27.6 kPa (4.0 psi), both of which are higher than that of MP with a vapor pressure of 11.0 kPa (1.6 psi). C₆ to C₁₄ esters are expected to have lower vapor pressures than many of the prior art oxygenates. By replacing
25 higher vapor pressure prior art oxygenates with the lower vapor pressure esters according to the invention, gasoline blenders will be able to include a higher percentage of butanes and other lower value high vapor pressure gasoline blending streams, according to the invention, in finished motor gasoline while still meeting maximum regulatory RVP limits. The addition
30 of incremental butane is especially beneficial due to butane's high octane

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value, low cost and ability to influence the maximum RVP of a gasoline blend.

Another embodiment of the present invention includes using the low water solubility esters according to the invention as octane booster(s) in motor gasoline. The branched esters of the invention are expected to have relatively high octane and, therefore, are expected to increase the average octane of the final motor gasoline as represented by the formula: $(\text{Research Octane} + \text{Motor Octane})/2$. For example, methyl pivalate has a motor octane of 108.2 and a research octane of 111.7. The necessary octane number requirements can be obtained by addition of the invention's esters in addition to taking advantage of the octane benefit realized from addition of incremental butane allowed by the low RVP of the invention's esters.

An important characteristic of gasoline fuels is a fuel component's stability within the gasoline fuel. Fuel components that are relatively unstable have a tendency to form deposits and gums in fuel-powered engines themselves and in the various components that accompanies such engines. Esters generally have excellent thermal and oxidative stability characteristics. Many of the esters, according to the invention, are expected to have especially high stability within gasoline fuels. For example, MP is a very stable compound toward hydrolysis, oxidation and temperature. Therefore, MP will positively contribute to gasoline fuel stability.

The invention includes providing methods of reducing surface and subsurface water contamination. The method aids in reducing surface and subsurface water contamination due to the low solubility in water of the invention's esters as compared to prior art oxygenates. This embodiment provides a method for aiding in reducing subsurface and surface water contamination caused at least in part by production, distribution, storage and/or use of oxygenated fuels. The method

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comprises producing a gasoline fuel containing an ester for use in spark-ignition engines, wherein the ester has a solubility in water of less than about 15,000 mg/L at 20°C, preferably less than about 6,500 mg/L at 20°C, thereby reducing subsurface and surface water contamination
5 caused at least in part by production, distribution, storage and/or combustion of oxygenated fuels as compared to oxygenated fuels containing oxygenates with a water solubility of greater than about 15,000 mg/L at 20°C.

Gasoline components typically are volatile organic compounds
10 (VOC), which are involved in complex photochemical atmospheric reactions, along with oxygen and nitrogen oxides (NO_x) in the atmosphere under the influence of sunlight to produce ozone. Ozone formation is a problem in the troposphere (low atmospheric or "ground-based"), particularly in an urban environment, since it leads to the phenomenon of
15 smog. Since VOC emissions are a source of ozone formation, motor gasoline manufacture and formulation are currently regulated to attain ozone compliance. Historically, governmental regulation of motor gasoline has focused on limiting the volatility of motor gasoline sold in the United States. Currently, motor gasoline volatility is regulated through seasonally
20 limiting motor gasoline RVP. A listing of EPA's regulatory motor gasoline RVP limits is found at 40 C.F.R. 80.27, *Controls and Prohibitions on Gasoline Volatility*, the entirety of which is hereby incorporated by reference.

Various measurements of reactivity with respect to ozone formation
25 are known. For instance, reactivity can be measured in environmental smog chambers, or they may be calculated using computer airshed models. See, for instance, Dr. William P. L. Carter, "Uncertainties and Research Needs in Quantifying VOC Reactivity for Stationary Source Emission Controls", presented at the California Air Resources Board

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(CARB) Consumer Products Reactivity Subgroup Meeting, Sacramento, CA (October 17, 1995).

There has also been developed a " K^{OH} scale", which provides a relative scale of the reactivity of VOC with the OH radicals involved in the complex reactions that produce ozone. See, for instance, Picquet et al., *Int. J. Chem. Kinet.* 30, 839-847 (1998), Bilde et al., *J. Phys. Chem. A* 101, 3514-3525 (1997).

Numerous other reactivity scales are known and new reactivity scales are constantly being developed. Since this is a rapidly changing area of research, the most up-to-date information is often obtained via the Internet. One example is Airsite, the Atmospheric Chemistry International Research Site for Information and Technology Exchange, sponsored by the University of North Carolina and the University of Leeds, at <http://airsite.unc.edu>.

Another way to measure the reactivity of a chemical in ozone formation is by using a technique developed by Dr. Carter (*supra*) at the Center for Environmental Research and Technology (CERT), University of California at Riverside. The CERT technique measures "incremental reactivities", the incremental amount of ozone that is produced when the chemical is added to an already polluted atmosphere.

Two experiments are conducted to measure the incremental reactivity. A base-case experiment measure the ozone produced in an environmental smog chamber under atmospheric conditions designed to represent a polluted atmosphere. The second experiment called "the test case" adds the chemical to the "polluted" smog chamber to determine how much more ozone the newly added chemical produces. The results of these tests under certain conditions of VOC and nitrogen oxide ratios are then used in mechanistic models to determine the Maximum Incremental Reactivities (MIR), which is a measure of ozone formation by the chemical substance in question.

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The State of California has adopted a reactivity program for alternative fuels based on this technique and the EPA has exempted several compounds due to studies conducted by CERT. See, for instance, Federal Register 31,633 (June 16, 1995) (acetone), 59 Federal Register 50,693 (Oct. 5, 1994) (methyl siloxanes), and Federal Register 17,331 (April 9, 1998) (methyl acetate). CARB and EPA use a weight average MIR for regulatory purposes, wherein the weight average MIR of a composition is calculated by summing the product of the weight percent of each substance and its respective MIR value.

A list of compounds and their MIR values is available in the Preliminary Report to California Air Resources Board, Contract No. 95-308, William P.L. Carter, August 6, 1998. A table of known MIR values may be found on the internet at <http://helium.ucr.edu/~carter/index.html>. CERT obtains other incremental reactivities by varying the ratios of VOC and nitrogen oxides. A detailed explanation of the methods employed and the determination of incremental reactivities and MIR scale may be found in the literature. See, for instance, *International Journal of Chemical Kinetics*, 28, 497-530 (1996); *Atmospheric Environment*, 29, 2513-2527 (1995) and 29, 2499-2511 (1995); *Journal of the Air and Waste Management Association*, 44, 881-899 (1994); and *Environ. Sci. Technol.* 23, 864 (1989). Moreover, various computer programs to assist in calculating MIR values are available, such as the SAPRC97 model, at <http://helium.ucr.edu/~carter/saprc97.htm>.

Any of these aforementioned scales could be used for regulatory purposes, however the MIR scale has been found to correlate best to peak ozone formation in certain urban areas having high pollution, such as the Los Angeles basin. MIR values can be reported as the absolute MIR determined by the CERT method or as a relative MIR. One common relative MIR scale uses the Reactive Organic Gas (ROG) in the base case as a benchmark. The Absolute Reactivity ROG is 3.93g O₃ per gram

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ROG. This value is then the divisor for the Absolute MIR of other VOCs, if MIR is cited relative to ROG. Absolute reactivities related to the ROG with the above-mentioned absolute reactivity 3.93g O₃ per gram are provided in "Updated Maximum Incremental Reactivity Scale for Regulatory Applications", Preliminary Report to California Air Resources Board, Contract No. 95-308, William P. Carter, August 6, 1998. For the purposes of this invention and specification, unless otherwise specifically stated, all MIR values provided herein are Absolute MIR values. It is understood, however, that the Absolute MIR values can be converted to Relative MIR and back to Absolute MIR by division or multiplication of MIR by ROG.

Most current regulations based on VOC emissions do not take into consideration the wide difference in ozone formation among non-exempt VOC compounds. For example, two non-exempt VOC compounds can have dramatically different ozone formation characteristics. Accordingly, most current regulations do not encourage end users to minimize ozone formation by using low reactivity hydrocarbon compositions.

Hydrocarbon compounds currently viewed as essentially non-ozone producing are those which have reactivity rates in the range of ethane. Ethane has a measured reactivity based on the MIR method of 0.35. In fact, the EPA has granted a VOC exemption to certain solvents with reactivity values in this range including acetone (MIR=0.48) and methyl acetate (MIR=0.12).

However, the number of known materials having reactivities of 0.50 or less based on the MIR scale is relatively small. Moreover, it is a discovery of the present inventors that many, if not most of the known fluids having acceptable reactivities with respect to ozone formation, have other unfavorable performance characteristics. For example, tertiary-butyl acetate (t-butyl acetate) has an excellent MIR=0.21, but has limited thermal stability. Generally, thermal stability is a substance's resistance to chemical decomposition under elevated temperatures.

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Table 1 demonstrates the extremely low relative reactivity – significantly lower than both acetone and ethane – of methyl pivalate. Table 1 shows the relative ozone impacts calculated for methyl pivalate for the various Empirical Kinetic Modeling Approach (EKMA). See Carter, *Development of Ozone Reactivity Scales for Volatile Organic Compounds*, 44 J. Air & Waste Mgt. Assoc. pp. 881-899 (Jan. 20, 1994). Similar data for ethane and acetone are shown for comparison. The ozone impacts are quantified by the effect of the compounds on peak ozone yields or on maximum 8-hour average ozone concentrations, relative to the average of all emitted volatile organic compounds (VOC) in units of ozone formed per mass of VOC emitted. This data shows that methyl pivalate satisfies the EPA requirements for organic compounds exempted from the list of ozone forming VOC's. Therefore, MP would be considered as an extremely low reactivity compound for any possible future reactivity based rules regarding gasoline formulation.

TABLE 1

Summary of calculated incremental reactivities (gram basis) for ethane, acetone and methyl pivalate, relative to the average of all VOC emissions.

Scenario	Ozone Yield Relative Reactivities			Max. 8 Hour Avg. Relative Reactivities		
	Ethane	Acetone	Me-Pvat	Ethane	Acetone	Me-Pvat
Max React	0.09	0.12	0.06	0.08	0.15	0.07
Max	0.16	0.14	0.11	0.10	0.15	0.09
Equal	0.21	0.15	0.12	0.12	0.15	0.09

20

In Table 1, the term "Max React" refers to a scenario derived by adjusting the NO_x emissions in a base case scenario to yield the highest incremental reactivity of the Base ROG Mixture. The Base ROG Mixture is the mixture of reactive organic gases (ROG's) initially present or emitted in the EKMA scenarios except for biogenic VOCs, VOCs present aloft, or VOCs added for the purpose of calculating their incremental reactivities. "Max Ozone" is a scenario derived by adjusting the NO_x emissions in a

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base case scenario to yield the highest peak ozone concentration. "Equal Benefit" is a scenario derived by adjusting the NO_x emissions in a base case scenario so VOC and NO_x reductions are effective in reducing O₃. See Carter, *Development of Ozone Reactivity Scales for Volatile Organic Compounds*, 44 J. Air & Waste Mgt. Assoc. pp. 881-899 (Jan. 20, 1994).

Table 2a shows the conversion of a portion of the data in Table 1 into Absolute MIR for methyl pivalate. As seen from Table 2a, Absolute Ozone Formation for different levels of NO_x in ROG is highest for highest level of NO_x scenario (MIR) and lowest for lowest level of NO_x scenario (EBIR). As a result, Absolute Reactivity in atmospheric photochemical ozone formation for tested compounds is highest for MIR scenario and lowest for EBIR scenario. Additionally Table 2b shows methyl pivalate as having an acceptable flash point, boiling temperature, RVP, low toxicity, good solvency and overall outstanding performance as versatile environmentally preferred exempt, extremely low ozone formation substance for a very wide range of applications.

Table 2a – Absolute Reactivity Conversion Ratios

		ROG	Ethane	Acetone	MP
Ozone Yield Relative Reactivities	MIR	1	0.09	0.12	0.06
	MOIR	1	0.16	0.14	0.11
	EBIR	1	0.21	0.15	0.12
Ozone Yield Absolute Reactivities (gm ozone/ gm compound)	MIR	3.93	0.354	0.472	0.236
	MOIR	1.41	0.226	0.197	0.155
	EBIR	0.82	0.172	0.123	0.098

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Table 2b – Compound Properties

		Acetone	MP
Boiling Temperature, °C		56	99
Viscosity (cps, 20°C)		0.33	0.74
Specific Gravity		0.792	0.873
Surface Tension		22.3	23.8
Flash Point (°C)		-20 *	6
Evaporation Ratio to Butyl Acetate		18	2.2
Hansen Solubility Parameter [cal ^{1/2} /cm ^{3/2}]	Total	9.2	8.1
	Nonpolar	7.6	7.2
	Polar	5.1	1.8
	H-Bonding	3.4	3.1
Toxicity (LD-50, mg/kg)		5800	6600

* Reflects Varied Reported Literature Data

The compounds presented in Table 3 show calculated Absolute MIR reactivities for acetone and methyl pivalate. These substances provide favorable MIR reactivities and appropriate solvency and compatibility with other gasoline components.

Table 3 – Calculated Absolute MIR Reactivities For Negligibly Polluting Potential Fluids

Compound	Absolute MIR (gram ozone produced/gram fluid)
Methyl Pivalate	0.236 (Actual measured value)
Tertiary-Butyl Pivalate	0.324

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The invention includes a method of reducing atmospheric ozone formation. There currently are two approaches to evaluation of the factors influencing ground-level ozone formation. One is based on the total amount of organics emitted into the atmosphere, which ultimately combine with nitrogen oxides in a photochemical reaction to form ozone. Based upon this, all organics are treated equivalently and all contribute equally to ozone formation, and for gasoline, RVP is used as the parameter

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correlating with the amount of total organics released into the air through evaporative pathways. The second approach recognizes that in fact there are significant differences (as much as about two orders of magnitude) in ozone formation for different compounds. Thus, the first approach is not
5 scientifically as useful as the second approach. To measure specific ozone formation for individual compounds, a method known as Maximum Incremental Reactivity (MIR) is employed. MIR is defined as gram ozone formed under atmospheric photochemical reaction conditions per gram of test substance (compound). Thus, the preferred oxygenated compositions
10 of the instant invention are products whose Absolute MIR is below 1.5g O₃ per gram of compound (low), preferably below 1.0g O₃ per gram of compound (very low) or most preferably below 0.5g O₃ per gram of compound (negligible).

The method, therefore, includes producing a gasoline fuel
15 containing an ester for use in internal combustion engines, wherein the ester has a RVP of less than about 4 pounds per square inch. An important factor in determining a substance's ozone formation potential includes the substance's vapor pressure. Compounds with relatively high vapor pressures are more likely to volatilize into the atmosphere from
20 open sources. Potential open sources include, for example, sources from production, distribution, storage and/or combustion of fuels containing oxygenates. The C₆ to C₁₄ esters according to the invention are expected to have very low vapor pressures in comparison to MTBE and some other oxygenates. Preferably, the esters have a RVP of less than about 3.5 psi.
25 More preferably, less than about 3.0 or 2.0 psi. For example, methyl pivalate has a RVP of about 1.6 psi.

The invention includes a second method for reducing atmospheric ozone formation. The method comprising producing a gasoline fuel containing an ester for use in spark-ignition engines, wherein the ester has
30 an Absolute MIR of less than about 1.5g O₃ per gram of ester, thereby

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reducing atmospheric ozone formation caused at least in part by production, distribution, storage and/or combustion of oxygenated fuels as compared to oxygenated fuels containing oxygenates that are photochemically reactive. Preferably, the ester has an Absolute MIR of less than about 1.0 or 0.5g O₃ per gram of ester. Certain hydrocarbon compounds have little or no potential to participate in photochemical reactions that result in ozone formation. Well known examples include methane and ethane, which are not considered as photochemically reactive compounds. When a reactivity scale for ozone formation is employed to estimate ozone formation, the contribution to ozone formation derived from the esters of this invention are very small, significantly below that of currently employed oxygenates such as MTBE (Absolute MIR = 1.35), TAME (Absolute MIR = 3.07), and ethanol (Absolute MIR = 1.92). This advantage enables the gasoline blender to have a wide range for oxygen content based on the esters of this invention, while meeting RVP requirements and still substantially reducing ozone formation through evaporative emissions. It may even be possible to formulate a gasoline using the esters of this invention having essentially no ozone forming potential as based on Absolute MIR values.

Many of the esters according to the invention, particularly the esters of lower neoacids, more particularly MP, provide very low reactivity toward ozone formation. Other esters of the invention are also expected to not participate appreciably in photochemical atmospheric reactions; therefore, many of the esters, according to the invention, can be considered environmentally preferred components for gasoline fuels. The following table contains the Absolute MIR for several compounds and is taken from W. P. Carter, *Updated Maximum Incremental reactivity Scale for Regulatory Applications*, Preliminary Rpt. to Calif. Air Res. Bd. Contract No. 95-308 (Aug. 6, 1998). The table displays the absolute MIR of some prior art oxygenates MTBE, ethanol and TAME, some esters of the

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invention methyl pivalate and methyl isobutyrate, some prior are aromatic gasoline compounds xylene and trimethyl benzene, and for butane. The esters of the invention have a very low MIR as compared to the prior art oxygenates and gasoline aromatic compounds.

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Table 4 - Absolute MIR of Selected Compounds

Compound	Absolute MIR (gram ozone/gram compound)
Methyl Isobutyrate	0.42
Methyl Pivalate	0.236
MTBE	1.35
TAME	3.07
Ethanol	1.92
Xylene	7.81
Trimethyl Benzene	10.17
Butane	1.44

An important feature of MIR-based ozone formation is that compounds which have MIR values equal to or lower than that of ethane (acetone) are considered to be non-polluting in terms of ozone formation. These compounds are under current regulations considered as not contributing to ozone formation. Ethane has an absolute MIR of 0.35g O₃ per gram ethane. Acetone has been defined by the EPA as exempt under this definition and therefore is also excluded from consideration as a ozone forming compound. Acetone has an absolute MIR of 0.48 (W. P. L. Carter, Preliminary Report to California Air Resources Board under Contract No. 95-308, August 6, 1998). As Table 4 displays, MTBE has an absolute MIR of 1.34 grams ozone per gram of compound. Methyl pivalate, an ester according to the invention, has an absolute MIR of 0.236 grams ozone per gram of compound. Methyl pivalate's MIR is therefore lower than ethane at 0.35g O₃ per gram of compound. Therefore in a

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regulatory sense, methyl pivalate would be considered as a compound that does not contribute to ozone formation. Additionally, methyl isobutyrate has an absolute MIR of 0.42g O₃ per gram of compound.

The invention also includes a method for reducing rubber-seal deterioration in fuel-powered engines that combust oxygenated gasoline fuel. The method comprises producing a gasoline fuel containing an ester for use in fuel powered engines, wherein the ester has a total Hansen solubility parameter of less than about 8.5 [cal^{1/2}/cm^{3/2}]. Preferably, the ester has a total Hansen solubility parameter less than about 8.0 or 7.5 [cal^{1/2}/cm^{3/2}]. A compound's solvency can be measured by using the Hansen solubility parameters. MP has a solvency similar to toluene, a common gasoline component, and therefore it is expected that MP will not appreciably, negatively impact rubber parts, including seals.

The esters according to the invention may be prepared by techniques known in the art. Conventionally, an ester is produced by the reaction of dehydration in which a carboxylic acid and an alcohol are heated in the presence of a catalyst, normally an acid catalyst. Examples of this type of ester preparation are found in Organic Chemistry by Morrison and Boyd, pp. 827-829 (4th ed. 1983) and U. S. Pat. No. 4,332,738 to Benitez et al. The esters of the invention may also be produced by reaction of olefins, carbon monoxide and an alcohol as disclosed by U.S. Pat. No. 5,463,095 to Shiokawa et al.

The esters, according to the invention, may also be prepared by techniques known in the art, including carbonyl insertion into alkyl ethers. U.S. Pat. No. 3,607,914 to Stouthamer discloses a process of producing esters by contacting an ether with carbon monoxide in the presence of a water-containing liquid hydrogen fluoride catalyst. U.S. Pat. No. 2,913,489 to De Benedictis et al. discloses a process for the production of esters from carbon monoxide and ethers with the aid of concentrated sulfuric acid as a catalyst.

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Example I

A blend of methyl pivalate was prepared according to ASTM D-2699 and D-2700. The resulting mixture was run on an octane engine according to ASTM D-2699 and D-2700 to determine the research and motor octane of methyl pivalate. A sample of methyl pivalate was also analyzed according to ASTM D-5191 to determine MP's Reid Vapor Pressure. The methyl pivalate results are included in Table 4a. The same procedures were employed to analyze methyl isobutyrate with the results presented in Table 5.

The results of the testing are presented in the following table:

Table 4a - Methyl Pivalate

Property	Result
Research Octane Number (RON)	111.7
Motor Octane Number (MON)	108.2
(RON+MON)/2 (calculated)	110.0
Reid Vapor Pressure at 100°F, psi	1.6

Table 5 - Methyl Isobutyrate

Property	Result
Research Octane Number (RON)	111.6
Motor Octane Number (MON)	103.1
(RON+MON)/2 (calculated)	107.4
Reid Vapor Pressure at 100°F, psi	2.60

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Example II

The thermal stability of methyl pivalate was tested at 200°C to 300°C. A 20-wt. % solution of MP in isopropyl alcohol was tested. The solution was subjected to GC port temperatures between 200°C to 300°C with a residence time of 0.6 seconds. A 0.2 μ l sample of each solution was injected into a Hewlett Packard 5890GC onto a 30M SPB-1 boiling point capillary column. The oven temperature was programmed from – 20°C to 310°C, with oven temperature ramps of 5°C and 10°C. The MP did not decompose during the test. The results are shown in the following table:

Table 6

Temp.	Peak A	Pivalic Acid	MeOH	MP	IPA
200°C	0.0	0.0	0.0	17.59	82.41
250°C	0.05	0.0	0.0	16.73	83.2
300°C	0.16	0.0	0.0	15.48	84.35

Example III

The water solubility of motor gasoline components and oxygenates was investigated for four motor gasoline mixtures containing no oxygenates (base gasoline), ethanol, methyl pivalate and MTBE. In each experiment, the motor gasoline sample, including a respective oxygenate, was mixed with a stated volume of water and the water phase was subsequently analyzed over time by GC to determine the amount and type of species dissolved in the water phase.

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The amount of oxygenate in the gasoline used in the experiment was determined to be 2.0 wt% for samples containing ethanol or methyl pivalate and 2.7 wt.% for samples containing MTBE. The amount of oxygenate added to the motor gasoline was calculated as follows:

$$\frac{\text{Molecular wt. of Compound}}{\text{Molecular wt. of Oxygen}} \times \% \text{ Oxygenate} = \chi ;$$

where: χ = # of grams oxygenate needed

then: $100 - \chi$ = grams of base gasoline

All samples have a base gasoline/oxygenate ratio to water of 10/5, 10/2.5 and 10/1. The components were added into do-pack jars, which had a rubber septa liner on its cap. The rubber septa was used to draw the water phase samples out via syringe and without losing any light hydrocarbons due to evaporation in the transfer. Samples were taken at 5 minutes, 1 hour, 3 hours, and 6 hours. The samples were shaken initially and then after each time interval when a sample was taken. Prior to taking the samples, a drop of Butyl Carbitol ($\approx 0.0150 - 0.0225$ grams) was added to a GC vial. The cap was then crimped. The water phase sample was then taken out of the do-pack jar via syringe and added into the crimped GC vial with Butyl Carbitol. Then the sample jar was vigorously shaken and allowed to stand for the next sample. After the sample was taken, it was loaded onto the auto-sampler to be injected into the HP-5890 GC. An auto-sampler was used to ensure a uniform injection size for each sample. Once all the gc scans were completed, the data points for the oxygenate, paraffins/olefins, xylene, benzene, and toluene were entered into a spreadsheet. Calculations have been made for ethanol and methyl pivalate at 2.0 wt. % oxygenate level and MTBE at 2.7 wt. % oxygenate level. The procedure was also used for an oxygenate-free base gasoline.

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Base Gasoline Composition

22% Aromatics (Benzene/Toluene = 1/5.8)

<10ppm Sulfur

≈0.5% Olefins

5 GC Conditions:

HP-5890

Column used: HP-1 30m, 0.25mm, 0.25μm

Column Flow – 1.05cc/min

Split vent – 105cc/min

10 Split ratio – 10/1

Air Flow – 320cc/min

H₂ Flow – 31cc/min

He Flow – 33.3cc/min

Initial Temp. – 50°C

15 Final Temp. – 300°C

Run Time – 60 min

Temp Program Rate – 10°/min

Attn – 2↑4

Sample size - 2μl

20

Relative Response Factors

An experiment was carried out to determine the relative response factor for oxygenates, paraffins/olefins, m-xylene, benzene, and toluene. The results were as follows:

25

Chemical	Relative Response Factor
Butyl Carbitol	1.0000
Ethanol	1.3649
Methyl Pivalate	1.0627
MTBE	0.8665
Benzene	0.5565
Toluene	0.5783
Paraffins/Olefins	0.5489
M-Xylene	0.5791

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The relative response factor was used to calculate the amount of chemicals in the water phase. The following tables contain the data, the amount, in parts per million (ppm), of each listed component that was found to be present in the water phase at a given time from initial mixing.

- 5 The calculations used to obtain the amount of each listed component in parts per million (ppm) level were two fold. First, the following equation was used to obtain the solubility in grams:

$$\text{Solubility (grams)} = \frac{(\text{weight internal standard}) \times (\text{area of hydrocarbon}) \times (\text{RRF Hydrocarbon})}{(\text{area of internal standard}) \times (\text{RRF internal standard})}$$

10

RRF – Relative Response Factor

Once the solubility of each component was found in grams, it was then converted to parts per million (ppm) by the following equation:

$$\text{Solubility (ppm)} = \frac{\text{Solubility (grams)}}{\text{amount of water used in sample (grams)}} \times 1,000,000$$

15

The term Paraffins/Olefins includes all hydrocarbons in the water phase except the other components that are listed. The title of each table contains the return of water to motor gasoline used in each experiment.

20

5/10 Water to Gasoline – Base Gasoline

Component	T=5min.	T=1hr.	T=3hr.	T=6hr.
Paraffins/Olefins	85	65	61	50
Benzene	9	12	14	13
Toluene	14	19	20	20
M-Xylene	7	10	12	13
Total:	117	108	108	99

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2.5/10 Water to Gasoline – Base Gasoline

Component	T=5min.	T=1hr.	T=3hr.	T=6hr.
Paraffins/Olefins	98	75	77	98
Benzene	14	15	20	21
Toluene	22	21	24	23
M-Xylene	11	10	11	10
Total:	146	123	132	154

1.0/10 Water to Gasoline – Base Gasoline

5

Component	T=5min.	T=1hr.	T=3hr.	T=6hr.
Paraffins/Olefins	318	210	241	219
Benzene	16	25	33	38
Toluene	43	45	40	46
M-Xylene	19	17	18	38
Total:	398	297	332	343

5/10 Water to Gasoline w/2.0 wt. % Ethanol

Component	T=5min.	T=1hr.	T=3hr.	T=6hr.
Paraffins/Olefins	8	34	43	46
Benzene	15	14	15	15
Toluene	20	23	24	22
M-Xylene	8	12	15	14
Ethanol	9963	11615	11031	11073
Total:	10017	11701	11129	11171

10

2.5/10 Water to Gasoline w/2.0 wt. % Ethanol

Component	T=5min.	T=1hr.	T=3hr.	T=6hr.
Paraffins/Olefins	10	49	61	55
Benzene	27	23	24	23
Toluene	42	33	33	35
M-Xylene	10	16	20	17
Ethanol	25040	29394	15038	14826
Total:	251314	295176	151788	149581

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1.0/10 Water to Gasoline w/2.0 wt. % Ethanol

Component	T=5min.	T=1hr.	T=3hr.	T=6hr.
Paraffins/Olefins	56	61	61	57
Benzene	122	52	52	53
Toluene	197	65	67	71
M-Xylene	104	26	24	38
Ethanol	108528	100573	100149	98598
Total:	109009	100779	100355	98819

5/10 Water to Gasoline w/2.0 wt. % Methyl Pivalate

5

Component	T=5min.	T=1hr.	T=3hr.	T=6hr.
Paraffins/Olefins	58	65	62	63
Benzene	13	12	12	12
Toluene	19	20	23	20
M-Xylene	9	7	8	10
Methyl Pivalate	116	129	126	119
Total:	216	236	234	226

2.5/10 Water to Gasoline w/2.0 wt. % Methyl Pivalate

Component	T=5min.	T=1hr.	T=3hr.	T=6hr.
Paraffins/Olefins	36	44	46	50
Benzene	15	16	18	14
Toluene	19	19	19	17
M-Xylene	7	7	13	13
Methyl Pivalate	129	130	142	136
Total:	207	219	239	232

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1.0/10 Water to Gasoline w/2.0 wt. % Methyl Pivalate

Component	T=5min.	T=1hr.	T=3hr.	T=6hr.
Paraffins/Olefins	49	53	54	55
Benzene	18	19	18	17
Toluene	26	27	23	26
M-Xylene	12	13	14	14
Methyl Pivalate	146	154	157	148
Total:	253	269	268	263

5/10 Water to Gasoline w/2.7 wt. % MTBE

5

Component	T=5min.	T=1hr.	T=3hr.	T=6hr.
Paraffins/Olefins	4	6	6	6
Benzene	5	8	6	5
Toluene	6	8	7	7
M-Xylene	3	4	3	2
MTBE	965	1104	1018	998
Total:	985	1131	1042	1020

2.5/10 Water to Gasoline w/2.7 wt. % MTBE

Component	T=5min.	T=1hr.	T=3hr.	T=6hr.
Paraffins/Olefins	11	11	9	11
Benzene	11	10	9	12
Toluene	13	13	14	13
M-Xylene	7	6	8	6
MTBE	1463	1355	1295	1577
Total:	1507	1397	1337	1621

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1/10 Water to Gasoline w/2.7 wt. % MTBE

Component	T=5min.	T=1hr.	T=3hr.	T=6hr.
Paraffins/Olefins	30	27	23	18
Benzene	31	26	24	24
Toluene	45	34	33	33
M-Xylene	25	23	21	23
MTBE	2777	2465	2360	2601
Total:	2909	2576	2463	2701

Note: Total may not be sum of the components' values listed due to truncation of the component totals.

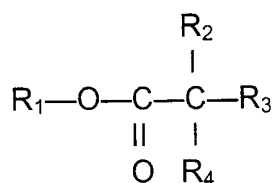
- 5 These and other embodiments of the invention will be apparent to one of skill in the art and are intended to be within the scope of the invention. All references cited in the present application are incorporated by reference in their entirety.

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CLAIMS:

What is claimed is:

- 5 1. A motor gasoline fuel comprising an ester, wherein said ester has a solubility in water of less than 15,000 mg/L at 20°C and said fuel has an overall solubility in water of less than 5,000 mg/L at 20°C.
2. A fuel as claimed in claim 1, wherein said ester has a solubility in
10 water of less than 6,500 mg/L at 20°C and said fuel has an overall solubility in water of less than 3,000 mg/L at 20°C.
3. A fuel as claimed in claim 2, wherein said ester has a solubility in water of less than 5,000 mg/L at 20°C.
- 15 4. A fuel as claimed in claim 3, wherein said ester has a solubility in water of less than 3,000 mg/L at 20°C.
5. A fuel as claimed in any of claims 1 through 4, wherein said ester
20 has the structural formula:



25 wherein R₁ is selected from the group consisting of methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, neopentyl and 3,5,5-trimethyl hexyl; R₂ is selected from the group consisting of hydrogen, methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, n-pentyl, isopentyl and neopentyl; R₃ is selected from the group consisting of
30 hydrogen, methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, n-

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pentyl, isopentyl and neopentyl; and R₄ is selected from the group consisting of methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, n-pentyl, isopentyl and neopentyl; and wherein said R₂, R₃, and R₄ contain a total of 2 to 11 carbon atoms.

5

6. A fuel as claimed in any of claims 1 through 5, wherein said fuel has an overall water solubility of less than 800 mg/L at 20°C.

7. A fuel as claimed in any of claims 1 through 6, wherein said fuel
10 has an overall water solubility of less than 500 mg/L at 20°C.

8. A fuel as claimed in any of claims 1 through 7, wherein said fuel has an overall water solubility of less than 300 mg/L at 20°C.

15 9. A fuel as claimed in any of claims 1 through 8, wherein said ester provides greater than 1.5 weight percent of oxygen to said fuel.

10. A fuel as claimed in any of claims 1 through 9, wherein said ester is methyl pivalate.

20

11. A method for reducing subsurface and surface water contamination, said method comprising producing a gasoline fuel containing an ester as claimed in any of claims 1 through 10 for use in fuel powered spark-ignition engines, thereby reducing subsurface and surface
25 water contamination caused at least in part by production, distribution, storage and/or use of oxygenated fuels as compared to oxygenated fuels containing oxygenates with a solubility in water of greater than 15,000 mg/L at 20°C.

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12. A method for reducing subsurface and surface water contamination caused at least in part by production, distribution, storage and/or use of oxygenated fuels, said method comprising producing a gasoline fuel containing an ester as claimed in any of claims 1 through 10 and a step
5 selected from the group consisting of:

- (a) storing said produced fuel in above-ground and underground liquid storage tanks;
- 10 (b) delivering said produced fuel to distribution points;
- (c) dispensing said produced fuel from said distribution points into fuel-powered vehicles; and
- 15 (d) combusting said produced fuel in spark-ignition engines located on said fuel-powered vehicles;

thereby reducing subsurface and surface water contamination as compared to oxygenated fuels containing oxygenates with a water
20 solubility of greater than 15,000 mg/L.

13. A method of producing lower cost oxygenated gasoline fuels compliant with the applicable maximum regulatory RVP limit for said fuel, said method comprising:

- 25 (a) adding an ester to a gasoline blend stock, wherein said ester contains 5 to 14 carbon atoms and has a RVP of less than 4 pounds per square inch; and
- (b) adding at least one lower cost gasoline blending component
30 selected from butane, isobutane, and isopentane to said

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gasoline blend stock, wherein said lower cost gasoline blending component has a RVP of greater than the maximum regulatory RVP of limit for said unleaded gasoline fuel.

5

14. A method for reducing atmospheric ozone formation, said method comprising producing a gasoline fuel containing an ester for use in spark-ignition engines, wherein said ester has a RVP of less than 4 pounds per square inch, thereby reducing atmospheric ozone formation caused at
10 least in part by production, distribution, storage and/or combustion of oxygenated fuels as compared to oxygenated fuels containing oxygenates with a RVP of greater than 4 pounds per square inch.

15. A method for reducing atmospheric ozone formation, said method
15 comprising producing a gasoline fuel containing an ester for use in spark-ignition engines, wherein said ester has an Absolute MIR of less than 1.5 gram ozone per gram of ester, thereby reducing atmospheric ozone formation caused at least in part by production, distribution, storage and/or combustion of oxygenated fuels as compared to oxygenated fuels
20 containing oxygenates having an Absolute MIR of greater than about 1.5 gram ozone per gram of ester.

16. A method as claimed in claim 15, wherein said ester has an Absolute MIR of less than 1.0 gram ozone per gram ester.

25

17. A method as claimed in claim 16, wherein said ester has an Absolute MIR of less than 0.5 gram ozone per gram ester.

18. A method for reducing the deterioration of rubber seals and other
30 rubber components in fuel distribution and combustion system in fuel-

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powered engines that combust oxygenated gasoline fuels, said method comprising producing a gasoline fuel containing an ester for use in said fuel-powered engines, wherein said ester has a total Hansen solubility parameter of less than $8.5 \text{ [cal}^{1/2}/\text{cm}^{3/2}]$, thereby reducing rubber-seal
5 deterioration in said fuel-powered engines as compared to oxygenated fuels containing oxygenates with a total Hansen solubility parameter of greater than $8.5 \text{ [cal}^{1/2}/\text{cm}^{3/2}]$.

19. A method as claimed in claim 18, wherein said ester has a total
10 Hansen solubility parameter of less than $8.0 \text{ [cal}^{1/2}/\text{cm}^{3/2}]$.

20. A method as claimed in claim 19, wherein said ester has a total Hansen solubility parameter of less than $7.5 \text{ [cal}^{1/2}/\text{cm}^{3/2}]$.