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(54) Titre : COMBUSTIBLE A FAIBLE TENEUR EN AZOTE AYANT UN POUVOIR LUBRIFIANT AMELIORE  
(54) Title: LOW NITROGEN CONTENT FUEL WITH IMPROVED LUBRICITY

(57) Abrégé/Abstract:

A hydrocarbon fuel is described comprising a hydrocarbon fuel boiling in the gasoline boiling range containing not greater than about 5 wppm nitrogen. The lubricity of such fuel is improved by the addition thereto of ethanol.



ABSTRACT OF THE DISCLOSURE

A hydrocarbon fuel is described comprising a hydrocarbon fuel boiling in the gasoline boiling range containing not greater than about 5 wppm nitrogen. The lubricity of such fuel is improved by the addition thereto of ethanol.

**BACKGROUND OF THE INVENTION****FIELD OF THE INVENTION**

This invention relates to hydrocarbon fuels of low nitrogen content suitable for use in spark ignition internal combustion engines and to the improvement in the lubricity for such low nitrogen fuel.

**SUMMARY OF THE INVENTION**

Hydrocarbon fuel of low nitrogen content, useful in spark ignition internal combustion engines, containing fuel system assemblies requiring lubrication, such as submerged fuel pumps and/or fuel injectors has unexpectedly been found to have its lubricity improved by the addition thereto of a minor quantity of ethanol.

**DETAILED DESCRIPTION OF THE INVENTION**

Hydrocarbon base fuel for use as a major component in a gasoline blend, useful in spark ignition internal combustion engines, boiling in the gasoline boiling range and having a low nitrogen content, in the range of about 5 wppm or less nitrogen (exclusive of nitrogen attributable to additives) has been found to have poor lubricity qualities.

Some nitrogen compounds present in typical base gasoline serve as natural lubricants to protect moving parts in fuel systems and engines not otherwise lubricated by the usual lubricating oil system. Reduction in the amount of such nitrogen compounds has been observed to be accompanied by a reduction in the lubricity of the base gasoline.

It has surprisingly been found that the lubricity characteristics of hydrocarbon base fuel useful as base gasoline and boiling in the gasoline boiling

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range and containing about 5 wppm nitrogen or less, preferably about 3 wppm nitrogen or less, more preferably about 2 wppm nitrogen or less, most preferably 0.5 wppm nitrogen or less as determined by method ASTM D 4629-96 are improved by blending such hydrocarbon base fuel with ethanol. Preferably at least about 2 vol% ethanol, more preferably at least about 5 vol% ethanol, still more preferably about 5 to 15 vol% ethanol based on the total volume of the blended fuel will be employed. The hydrocarbon fuel blend of the present invention will generally contain about 20 vol% or less ethanol, thus preferably about 2-20 vol% ethanol, more preferably about 5-20 vol% ethanol, still more preferably about 5 to 15 vol% ethanol will be used. This effect on lubricity is unexpected and is contrary to the decrease in lubricity that results from the addition of ethanol to base gasoline containing a greater amount of nitrogen compounds boiling in the gasoline boiling range.

Hydrocarbon base fuel suitable as base gasoline in the present invention preferably also has low volatility and low sulfur to reduce emissions and meet current and future regulatory targets.

By low sulfur is meant a sulfur content of the hydrocarbon base fuel of about 50 wppm or less, preferably about 10 wppm or less, more preferably less than about 10 wppm, most preferably less than about 5 wppm as determined by test method ASTM D 5453-93.

The base fuel useful in the present invention is preferably characterized in that the nitrogen to sulfur weight ppm ratio is about 0.01:1 to 1:1, preferably about 0.02:1 to 0.5:1, still more preferably about 0.03:1 to 0.5:1.

It is well known that ethanol increases volatility of the fuel composition when splash blended into gasoline due to deviation from Raoult's

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Law (SAE Automotive Fuels Handbook, 1990, Chapter 11). In the present invention therefore, the Reid Vapor Pressure (RVP) of the base gasoline, prior to introduction of ethanol is preferably less than about 9 psi, more preferably less than about 8 psi and most preferably less than about 7 psi. RVP as used herein and in the claims refers to the dry vapor pressure equivalent as determined by Institute of Petroleum method IP 394.

The hydrocarbon base fuel is useful in spark ignition internal combustion engines and boiling in the gasoline boiling range and can be either leaded, additized with octane enhancing manganese compounds, or unleaded gasoline of any grade. Preferably, the fuel is unleaded gasoline of the aforesaid low nitrogen content level.

Base gasoline of the recited low nitrogen content can be produced by those skilled in the gasoline refining art using any technique known to be effective for the reduction of organic nitrogen present in hydrocarbon streams. Such techniques include methods such as adsorption using selective adsorbents, and catalytic hydrodenitrogenation.

The fuel composition comprising the base gasoline and ethanol typically will contain additives including detergents, deicing additives, anti-knock additives (other than lead compounds), anti-corrosion additives, other anti-wear/lubricity improving additives, anti-oxidants, anti-rust additives, etc. These can be added separately or in combination in one or more steps in any order to the fuel composition or any of its components. The term additive is meant to include any chemical added at any stage during the processing or blending of the fuel.

Suitable additives include, by way of example and not limitation, as, antioxidants, the aromatic diamines and alkyl phenols; as metal deactivators,

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N,N'disalicylidene-1,2 propane diamine, to deactivate any copper present in the gasoline; as corrosion inhibitors, polar molecules such as tall oil fatty acids/esters, esters or amine salts of alkenyl succinic acids, alkyl ortho-phosphoric acids, alkyl phosphoric acids, aryl sulfonic acids; as biocides, various boron compounds, quaternary ammonium salts of salicylic acid, glycol ethers, etc.; anti static agents; as drag reducing agents, various high molecular weight polymers that shear readily and thus reduce drag; demulsifiers and dehazers; as anti-icing additives, various C<sub>3</sub>+ alcohols or glycols; surfactant additives such as amines or imidazoline salts of carboxylic or alkyenyl succinic acids which also function as antiwear additives; as detergents, alkyl amine phosphates or fatty acid amides, alkenyl succinimides, polybutene amines and polyether amines; polymeric dispersants; other nitrogen compounds such as nitrogen containing octane enhancers, e.g., aniline or its derivatives, or other organic amines. In addition, different carrier fluids or diluents can be used, including mineral oil, light aromatic solvents, esters such as polyol ester, or polymeric material such as polyolefins, polyethers or polyglycols. Other additives that can be present in gasoline include various anti knock additives, anti octane requirement increase additives, anti pre-ignition or misfire additives, flame front accelerants, spark aid additive, anti valve seat recession additives, upper cylinder head lubricants, anti wear additives and anti sludge additives, all of which are types of materials well known in the gasoline formulation art.

The present fuel comprising gasoline having a nitrogen content of about 5 wppm or less and containing at least 2 vol% ethanol is especially useful in fueling internal combustion engines containing fuel system assemblies requiring lubrication such as submerged fuel pump and fuel injectors.

The ethanol used can be derived from any source, e.g., by direct synthesis, or by production from renewal resources, e.g., grain, etc., by

fermentation and distillation. It is preferred that the ethanol be fuel grade ethanol as defined in, for example, ASTM D 4806-98.

The present invention is further illustrated by the following examples and comparative examples which are not, however, to be construed as limitations thereof.

### EXAMPLES

The data in Table 1 demonstrate in Example 1 that ethanol improves gasoline lubricity, as measured by friction coefficient, when nitrogen is less than about 5 wppm. The nitrogen content was measured according to ASTM D 4629-96 (employing Antek apparatus manufactured by Antek Instruments, Inc.). Sulfur content was measured using ASTM D 5453-93 (employing Antek apparatus manufactured by Antek Instruments, Inc.). The RVP was measured as the dry vapor pressure equivalent according to Institute of Petroleum method IP 394 (employing a Setavap Analyzer manufactured by Stanhope-Seta). The data were generated using the HFRR friction and wear test. The HFRR test procedure employed was a modification of European standard test CEC F-06-A-96 for diesel fuels modified for gasoline in that the test is run at 25°C (as opposed to 60°C in the diesel test) and a cover is placed over the test cell to reduce evaporation of the gasoline sample under test. Data are also included, Comparative Examples 1 and 2, on two other gasoline samples with nitrogen content of 5.5 wppm and 18 wppm, respectively. Ethanol does not improve lubricity of these fuels. This demonstrates that ethanol improves lubricity in gasoline when nitrogen content is about 5 wppm or less.

Example 2 was run using a different base gasoline than Example 1 and further demonstrates that the addition of ethanol to a base gasoline of low nitrogen content improves the lubricity of such fuel.

TABLE 1

		<u>Ethanol (Vol%)</u>	<u>Friction</u>
<u>Example 1</u>	<u>Gasoline</u> Sulfur = 9 wppm; Nitrogen = 0.3 wppm; RVP = 7.4 psi 100 vol% 95 vol% 90 vol%	0	0.486
		5	0.461
		10	0.412
<u>Comparative Example 1</u>	<u>Gasoline</u> Sulfur = 51 wppm; Nitrogen = 5.5 wppm; RVP = 11.3 psi 100 vol% 95 vol% 90 vol%	0	0.368
		5	0.379
		10	0.43
<u>Comparative Example 2</u>	<u>Gasoline</u> Sulfur = 180 wppm; Nitrogen = 18 wppm; RVP = 10.6 psi 100 vol% 95 vol% 90 vol%	0	0.347
		5	0.342
		10	0.355
<u>Example 2</u>	<u>Gasoline</u> Sulfur = < 5 wppm; Nitrogen = 0.6 wppm; RVP = 11.1 psi 100 vol% 95 vol% 90 vol%	<u>Ethanol (Vol%)</u>	<u>Friction</u>
		0	.50
		5	.39
		10	.37

**CLAIMS:**

1. A method for improving the lubricity of hydrocarbon fuel boiling in the gasoline boiling range and for use in a spark ignition internal combustion engine comprising a base fuel having a base fuel nitrogen content of about 5 wppm or less nitrogen, exclusive of nitrogen attributable to additives, by adding to said fuel at least about 2 vol % ethanol.
2. The method of claim 1 wherein the fuel contains about 3 wppm or less of nitrogen.
3. The method of claim 1 wherein the fuel contains about 2 wppm or less of nitrogen.
4. The method of claim 1 wherein the fuel contains about 0.5 wppm or less of nitrogen.
5. The method of any one of claims 1 to 4 wherein the base fuel is further characterized as containing about 50 wppm or less of sulphur.
6. The method of any one of claims 1 to 4 wherein the base fuel is further characterized as containing about 10 wppm or less of sulfur.
7. The method of any one of claims 1 to 4 wherein the base fuel is further characterized as containing about 5 wppm or less of sulfur.
8. The method of any one of claims 1 to 4 wherein at least about 5 vol % ethanol is added to the fuel.
9. The method of any one of claims 1 to 4 wherein about 5 to 15 vol % ethanol is added to the fuel.
10. The method of claim 5 wherein at least about 5 vol % ethanol is added to the fuel.
11. The method of claim 6 wherein at least about 5 vol % ethanol is added to the fuel.

12. The method of claim 7 wherein at least about 5 vol % ethanol is added to the fuel.
13. The method of claim 5 wherein about 5 to 15 vol % ethanol is added to the fuel.
14. The method of claim 6 wherein about 5 to 15 vol % ethanol is added to the fuel.
15. The method of claim 7 wherein about 5 to 15 vol % ethanol is added to the fuel.
16. The method of claim 5 wherein the nitrogen to sulfur weight ppm ratio of the fuel is about 0.01:1 to 1:1.
17. The method of any one of claims 1 to 4 wherein the fuel is further characterized as having a Reid Vapor Pressure of less than about 9 psi.