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HYDROCARBON FUELS HAVING IMPROVED ANTIKNOCK PROPERTIES

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This invention relates to fuels, and more particularly to fuels with improved knock resistance when used over the entire operating range of internal combustion engines.

It is recognized that internal combustion engines knock under a wide variety of engine operating conditions, including varying speeds, degree of spark advance, compression ratio, fuel/air mixture ratio, temperatures, and intake manifold pressure. Because of these variations in engine conditions, the engine may knock under "mild" or "severe" stress. Industry recognizes that "mild" stress is usually encountered when the engine knocks under conditions of relatively low speed, retarded spark or low operating temperatures such as is normally experienced in the operation of the existing type passenger car. On the other hand, "severe" stress is encountered under conditions of high engine speeds, advanced spark, high operating temperatures or high manifold pressures such as encountered with high speed operation of automotive type engines or the normal operation of aviation engines.

The development of internal combustion engines of high compression ratios has established a need for high quality fuels having increased resistance to knock over the above mentioned wide range of engine operating conditions. Careful refining and blending of fuel components can produce a fuel of sufficiently increased knock resistance to satisfy the engine requirements under the previously mentioned conditions. Usually, however, tetraethyllead is today employed in these fuel blends to improve the knock resistance which cannot easily and economically be obtained through refining techniques. Tetraethyllead is widely used since it does impart improved antiknock quality over the wide range of engine conditions mentioned above. The use of tetraethyllead, however, has limitations. Each successive increment of tetraethyllead produces only a fraction of the improvement in antiknock rating obtained with each previous increment. Certain fuels for spark ignition engines, particularly those containing large proportions of aromatic and/or olefinic components, respond rather poorly to tetraethyllead, especially at the normal upper limit of 3 ml. of tetraethyllead per gallon in automotive engines, or 4.6 ml. per gallon in aviation engines.

It is an object of the present invention to provide new and improved antiknock compounds which function over the entire range of engine operating conditions. It is a further object of this invention to provide new and improved antiknock compounds for fuels already containing tetraethyllead, which increase knock resistance to a degree not attainable by the use of tetraethyllead alone. It is a still further object of this invention to provide antiknock compounds which are superior to tetraethyllead under severe operating conditions such as normally encountered in aircraft or in the newly proposed high compression automotive engines.

It has now been found that lithium salts of organic acyclic branched carboxylic acids, in which the carboxy group is attached to a methylene group in an aliphatic radical, are very effective antiknock compounds for fuels, when such fuels are used over the entire operating range of internal combustion engines. The acids to be used according to the present invention are preferably those containing from 5 to 18 carbon atoms including the carboxy group. The organic groups attached to the carbon atom adjacent to the carboxy group must be branched and acyclic.

The compositions of the present invention are particularly applicable for use in engines equipped with fuel injection systems, since with ordinary carburetion many of these additives are not sufficiently inductible to avoid deposition in the intake system over an extended period of operation. These compounds, however, are effective irrespective of the method by which they are introduced into the cylinder of the engine. While they are normally introduced with the fuel itself, they may be introduced separately as a dust or powder, or with solvents used either to carry them alone or in the supplementary antiknock solutions such as the water/alcohol mixtures employed in aircraft engines or tetraethyllead/alcohol mixtures employed in automotive engines.

In general the lithium compounds of the carboxylic acids employed in this invention may be prepared by reacting the appropriate acidic organic compound with lithium or lithium hydride, hydroxide, alkoxide or carbonate. The carboxylates are readily obtained on neutralizing the free acid with any lithium base, e.g., the hydroxide or carbonate, followed by recovery of the salt from solution (which may be in water, alcohol or in an inert organic solvent). Alternatively, they may be prepared by saponification of an ester with a lithium base. It is convenient to prepare the lithium compounds in aqueous systems, subsequently removing water by drum drying, spray drying or other conventional processes.

This invention is applicable to hydrocarbon fuels for internal combustion engines and more particularly to fuels which may be a mixture of hydrocarbons boiling in the gasoline range, or a refined gasoline as defined in the ASTM designation D288–53 (adopted 1939, revised 1953). The invention is especially useful in fuels of 40 performance number or higher such as those used in spark ignition engines of either automotive or aviation type over their entire range of operation.

The lithium salts employed in the present invention are effective in clear fuels and those fuels containing tetraethyllead in an amount up to 6.0 ml. of tetraethyllead per gallon. These fuels may be finished fuels which may contain varying amounts of conventional fuel additives such as scavenging agents, dyes, antioxidants, anti-icing agents; inhibitors for rust, corrosion, haze formation, gum formation; anti-preignition agents, etc.

The hydrocarbon fuels in which the additives of the present invention may be incorporated may contain blending agents to enhance the solubility of the lithium compounds of this specification in the fuel. Typical blending agents are those set forth in the examples, although other blending agents such as gasoline miscible alcohols, glycols, esters, ketones, amides, and other polar organic liquids may be used. The lithium salts may be dissolved directly in the blended gasoline or added as a concentrated solution in a blending agent.

The amount of lithium compound normally employed will of course vary with the quality and the intended end use of the fuel. Normally the amount of lithium compound employed will be sufficient to give from 0.005 gram to 2.0 grams of lithium per gallon of fuel, the preferred range being between 0.05 to 1.0 gram of lithium per gallon, regardless of the amount of tetraethyllead employed in the fuel. In contrast to the behavior of tetraethyllead, additional increments of these lithium compounds usually produce improvements in knock resistance approximating that obtained with the previous increment;

that is, a graph of the response of fuels to these additives will be substantially linear.

The lithium salts of acyclic branched chain carboxylic acids of from 5 to 18 carbon atoms improve the performance numbers of gasoline-type fuels when employed in the amounts specified above. In addition to those compounds employed in the specific examples, the lithium salts of other acids may be employed, such as: 3-methylpentanoic acid, 4,5-dimethylhexanoic acid, 3-ethylhexanoic acid, 3,4,4-trimethylpentanoic acid, 3,3,4,4-tetramethylpentanoic acid, 3-methylheptanoic acid, 4-tert. butylhexanoic acid, 6-methyl-3-isoamyl heptanoic acid and 6-methyl-3-propyl-3-isoamylheptanoic acid.

The lithium salts of primary acids in which branching is close to the carboxyl group are preferred since they exhibit greater antiknock activity than those in which branching is not remote. The preferred salts are derived from acids having at least 1 branch no more than 6 carbons removed from the carboxyl group. It is understood that mixtures of lithium salts of different acids may be employed.

To illustrate this invention, a number of examples are given in which comparisons show the effectiveness of the compounds of the present invention in clear and leaded fuels.

In the examples, three knock test methods were employed, the first two being representative of automotive operating conditions are referred to as the "mild" test and the "severe" test, while the third test is representative of supercharged aviation conditions. In the "mild" and "severe" tests, the fuel samples were tested in a Waukesha ASTM D909–49T Knock Test Method single cylinder knock rating engine equipped with a four-hole, overhead valve, variable compression ratio head. The engine is mounted on a test stand with a suitable motor-generator unit which absorbs the power output of the engine. A spark plug, mounted in the conventional position for this type engine, a rate of change of pressure pick-up and a steel plug occupy three of the four holes in the head. A Waukesha ASTM D909–49T Knock Test Method fuel injector is inserted into the fourth hole in the head by means of an adapter, and is supplied with fuel from the fuel injection pump. This fuel system injects the fuel directly into the combustion chamber. With the engine operating, the occurrence of knock is determined at the trace knock intensity level by means of the rate of change of pressure pick-up mounted in the cylinder head. The signal from the pick-up feeds into a cathode-ray oscilloscope and the occurrence of knock is observed as a shattering of the rate of change of pressure trace on the oscilloscope screen late in the engine cycle.

The engine is operated under the following conditions:

	Test Conditions	
	Mild	Severe
Speed, r.p.m.	600	1200
Spark advance (degree before top center)	13	30
Fuel injection timing (degree after top center on intake stroke)	50	50
Fuel/Air ratio	0.0800±0.0005	0.0700±0.0005
Intake manifold air pressure, (in. Hg abs.)	30	30
Coolant temperature, ° F.	212	212
Intake air temperature, ° F.	200	200
Oil temperature, ° F.	160	160
Compression ratio	Varied to produce trace knock	

Under these operating conditions, the knock resistance of all fuels tested in this specification is determined by comparing the highest useable knock-free compression ratio of these fuels to that of primary reference fuels consisting of blends of isooctane and n-heptane below 100 performance number, and isooctane plus tetraethyllead above 100 performance number. The knock resistance of all fuels tested is expressed in this specification in terms of Army-Navy Performance Numbers as defined in Tables VII and VIII in the ASTM Aviation Method (D614–49T), as recorded in the ASTM Manual of Engine Test Methods for Rating Fuels, published by the American Society for Testing Materials, October 1952.

These tests and the test conditions were developed to evaluate antiknock compounds under the same stresses as would be encountered in automotive operation.

The supercharged aviation tests were carried out in an engine equipped with manifold fuel injection in accordance with the procedure set forth in ASTM D–909–49T Knock Test Method. In the examples using this test method any performance number above 161, which is the present official rating limit according to the ASTM test, was obtained by direct linear extrapolation, which is an accepted method.

The following examples are given to illustrate the invention in which the percentages used are by volume unless otherwise specified.

Example 1

To a sample of gasoline comprising 34 vol. percent saturated hydrocarbons, 30 vol. percent olefins, and 36 vol. percent aromatic hydrocarbons, 3 ml. tetraethyllead per gallon and 4 vol. percent ethanol were added to make a fuel blend having a performance number of 110 in the mild test. To each of different samples a lithium salt of an organic acid was added to this fuel blend to produce a lithium concentration stated. As a result, the performance number of the fuel blend was raised to 118 by 0.25 g. of lithium per gallon as lithium 3-methylbutyrate, and to 117 by 0.25 gram of lithium per gallon as lithium 3,5,5-trimethylhexanoate in the mild test.

Example 2

To a blend of gasoline and ethanol, as described in Example 1, having a performance number of 110 in the mild test and 83 in the severe test, lithium 4-methylpentanoate was added to produce a lithium concentration of 0.28 g. per gallon. As a result, the performance number of the fuel blend was raised to 117 in the mild test and 91 in the severe test.

Example 3

To a blend of gasoline and ethanol as described in Example 2, lithium "isooctanoate," which had been prepared by the oxidation of a mixture comprising isomeric primary alcohols of eight carbons having substantially no branching on the 2-carbon, was added to produce a lithium concentration of 0.25 gram per gallon. As a result, the performance number of the fuel blend was raised to 121 in the mild test and 94 in the severe test.

Example 4

To a sample of aviation-type gasoline comprising 96.5% saturated hydrocarbons and 3.5% aromatic hydrocarbons, 4 ml. tetraethyllead per gallon and 5 vol. percent ethanol were added to make a fuel blend having a performance number of 108 in the mild test. Lithium 3-methylbutanoate was added to this fuel blend to produce a lithium concentration of 0.25 gram per gallon. As a result, the performance number of the fuel blend was raised to 120 in the mild test.

Example 5

To a sample of gasoline comprising 60 vol. percent saturated hydrocarbons, 24 vol. percent olefins, and 16 vol. percent aromatic hydrocarbons, 5 vol. percent of ethanol was added as a solubilizing agent to make a fuel blend having a performance number of 76 in the mild test. Lithium 3,3-dimethylbutanoate was added to this fuel blend to produce a lithium concentration of 0.65 gram per gallon. As a result, the performance number of the fuel blend was raised to 92 in the mild test.

Example 6

To a sample of isooctane, 5 vol. percent ethanol was added as a solubilizing agent to make a fuel blend having a performance number of 112 in the F–4 Supercharge test. To each of different samples of this fuel blend, a lithium salt was added to produce a lithium concentration stated.

As a result, the performance number of the fuel blend, as rated in the F–4 Supercharge test, was raised to over 161 by 0.13 gram of lithium per gallon as lithium 3-methylbutanoate, to over 161 by 0.13 gram of lithium per gallon as lithium 4-methylpentanoate, and to over 161 by 0.13 gram of lithium per gallon as the lithium isooctanoate which was described in Example 3.

Example 7

To a sample of isooctane, 0.5 vol. percent ethanol was added as a solubilizing agent to make a fuel blend having a performance number of 100 in the F–4 Supercharge test. Lithium 3,5,5-trimethylhexanoate was added to the fuel blend to produce a lithium concentration of 0.02 gram lithium per gallon; as a result, the performance number of the fuel blend was raised to 125 in the F–4 Supercharge test.

Example 8

To a sample of isooctane, 1.5 ml. tetraethyllead per gallon and 2.5 vol. percent ethanol was added to make a fuel blend having a performance number of 133 by the Supercharge rich test. Lithium 4-methylpentanoate was added to the fuel blend to produce a lithium concentration of 0.02 gram lithium per gallon; as a result, the performance number of the fuel blend was raised to 168 in the F–4 Superecharge test.

What is claimed is:

1. A hydrocarbon fuel of the gasoline boiling range containing a lithium salt of an acyclic hydrocarbon branched carboxylic acid, the carboxy group of said acid being attached to a methylene group in an aliphatic radical, in an amount sufficient to give from 0.005 gram to 2.0 grams of lithium per gallon of fuel.

2. A hydrocarbon fuel of the gasoline boiling range containing a lithium salt of an acyclic hydrocarbon branched carboxylic acid, the carboxy group of said acid being attached to a methylene group in an aliphatic radical, in an amount sufficient to give from 0.05 gram to 1 gram of lithium per gallon of fuel.

3. A hydrocarbon fuel of the gasoline boiling range containing tetraethyllead in an amount up to 6.0 ml. tetraethyllead per gallon and a lithium salt of an acyclic hydrocarbon branched carboxylic acid, the carboxy group of said acid being attached to a methylene group in an aliphatic radical, in an amount sufficient to give from 0.005 gram to 2.0 grams of lithium per gallon of fuel.

4. A hydrocarbon fuel of the gasoline boiling range containing tetraethyllead in an amount up to 6.0 ml. tetraethyllead per gallon and a lithium salt of an acyclic hydrocarbon branched carboxylic acid, the carboxy group of said acid being attached to a methylene group in an aliphatic radical, in an amount sufficient to give from 0.05 gram to 1 gram of lithium per gallon of fuel.

5. A method of operating an interenal combustion engine which comprises introducing a hydrocarbon fuel of the gasoline boiling range into the combustion chamber of the cylinder and simultaneously therewith introducing into said combustion chamber so that it is present at the time the fuel is ignited a lithium salt of an acyclic hydrocarbon branched carboxylic acid, the carboxy group of said acid being attached to a methylene group in an aliphatic radical, in an amount sufficient to give from 0.005 gram to 2.0 grams of lithium per gallon of fuel.

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