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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. A still further object of the invention is to produce new compounds which are effective antiknock agents for fuels.

It has now been found that lithium salts of organic

tertiary carboxylic acids, in which the carboxy group is attached to a carbon atom which has the remaining three valences attached to three other carbon atoms, are very effective antiknock compounds for fuels, when such fuels are used over the entire operating range of internal combustion engines.

The organic groups attached to the carbon atom adjacent to the carboxy group are hydrocarbon groups, that is, they contain only carbon and hydrogen, and they may be aliphatic, cycloaliphatic, or aromatic, and this carbon atom may be part of a ring system. 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 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 inductable 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 car. 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.

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 Examples I to IX, inclusive, fuel samples were tested under both mild and severe test conditions 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	1,200
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.

Example I

To each of two samples of a gasoline containing 3.0 ml. of tetraethyllead per gallon and 152 ml. of Cellosolve per gallon as a solubilizing assistant and having a performance number of 98 in the mild test and 80 in the severe test, lithium 1,3-dimethylcyclobutane carboxylate was added in quantities so that the blended gasoline contained 3.4 grams per gallon and 6.8 grams per gallon respectively. As a result the performance numbers were raised to 104 and 112 respectively in the mild test, and 88 and 97 respectively in the severe test.

Example II

(*a*) To each of two samples of a gasoline containing 3.0 ml. of tetraethyllead per gallon and 76 ml. of isopropanol per gallon as a solubilizing assistant and having a performance number of 108 in the mild test and 84 in the severe test, lithium 1,2,2,3-tetramethylcyclopentane carboxylate was added in quantities so that the blended gasoline contained 1.7 grams per gallon and 12.0 grams per gallon respectively. As a result the performance numbers were raised to 111 and 142 respectively in the mild test and to 88 and 99 respectively in the severe test. Concentrations of 3.4, 5.1, 6.8 and 8.5 grams per gallon of this lithium compound raised the performance number to 114, 120, 124 and 131 respectively in the mild test. In the severe test the performance numbers were raised to 90, 93, 95 and 97 respectively.

(*b*) To each of two samples of an unleaded gasoline (no tetraethyllead added) containing 76 ml. of isopropanol per gallon as a solubilizing assistant and having a performance number of 78 in the mild test and 66 in the severe test, lithium 1,2,2,3-tetramethylcyclopentane carboxylate was added in quantities so that the blended gasoline contained 1.7 grams per gallon and 17 grams per gallon respectively. As a result, the performance numbers were raised to 85 and 123 respectively in the mild test, and to 70 and 96 respectively in the severe test. Concentrations of 3.4, 5.1 and 8.5 grams per gallon of this lithium compound raised the performance numbers to 88, 92 and 102 respectively in the mild test. In the severe test performance numbers were raised to 73, 75 and 82 respectively.

Example III

To a sample of a commercial premium grade gasoline containing 3.0 ml. of tetraethyllead per gallon and 38 ml. of isopropanol per gallon as a solubilizing assistant and having a performance number of 96 in the mild test and 80 in the severe test, 6.4 grams of lithium 1,3,3-trimethylcyclohexane carboxylate per gallon was added. As a result, the performance numbers were raised to 104 in the mild test and to 88 in the severe test.

Example IV

To a sample of a gasoline containing 3.0 ml. of tetraethyllead per gallon and having a performance number of 97 in the mild test and 85 in the severe test, 7.9 grams of lithium 1,4-diisopropylcyclohexane carboxylate per gallon was added. As a result, the performance numbers were raised to 103 in the mild test and to 94 in the severe test.

Example V

(*a*) A gasoline containing 3.0 ml. of tetraethyllead per gallon and 76 ml. of ethanol per gallon had a performance number of 108 in the mild test and 85 in the severe test. To each of two samples of this gasoline (not containing ethanol) was added an ethanol solution of lithium 2,2-dimethylpropionate in such quantities that the finished blend contained 76 ml. of ethanol per gallon and 1.3 grams per gallon and 9.0 grams per gallon of the lithium compound respectively. As a result, the performance numbers were raised to 110 and 147 respectively in the mild test, and to 90 and 102 respectively in the severe test. Concentrations of 2.5 and 5.0 grams of this lithium compound per gallon raised the performance numbers to 114 and 125 in the mild test and 94 and 99 in the severe test.

(*b*) A gasoline containing 76 ml. of ethanol per gallon had a performance number of 75 in the mild test and 68 in the severe test. To each of two samples of this gasoline (not containing ethanol) was added an ethanol solution of lithium 2,2-dimethylpropionate in such quantities that the finished blend contained 76 ml. of ethanol per gallon and 0.6 gram and 10.6 grams of the lithium compound per gallon respectively. As a result, the performance numbers were raised to 79 and 121 respectively in the mild test, and to 70 and 91 respectively in the severe test. Concentrations of 1.8, 3.5 and 5.3 grams of this lithium compound per gallon raised the performance numbers to 83, 89 and 96 in the mild test and 74, 78 and 82 in the severe test.

Example VI

To a sample of a gasoline containing 3.0 ml. of tetraethyllead per gallon and 190 ml. of methanol per gallon as a solubilizing assistant and having a performance number of 103 in the mild test and 78 in the severe test, 6.4 grams of lithium 2,2-diethylhexanoate per gallon was added. As a result, the performance numbers were raised to 114 in the mild test and to 88 in the severe test.

Example VII

To a sample of a gasoline containing 3.0 ml. of tetraethyllead per gallon and 190 ml. of methanol per gallon as a solubilizing assistant and having a performance number of 102 in the mild test and 81 in the severe test, 6.4 grams of lithium 2-methyl-2-cyclohexylpropionate per gallon was added. As a result, the performance numbers were raised to 110 in the mild test and to 92 in the severe test.

Example VIII

To a sample of a commercial, regular grade gasoline containing 2.94 ml. of tetraethyllead per gallon and 76 ml. of isopropanol per gallon as a solubilizing assistant and having a performance number of 79 in the mild test and 72 in the severe test, 5.0 grams of lithium 1,2,2,3-tetramethylcyclopentane carboxylate per gallon was added. As a result, the performance numbers were raised to 84 in the mild test and 78 in the severe test. Utilizing these same gasolines in a Mercedes-Benz 300 SL automobile equipped with a fuel injection system, the gasoline containing only tetraethyllead and isopropanol had a performance number of 75 and the gasoline containing the lithium compound had a performance number of 80 when rated by the Modified Uniontown Procedure, CRC designation F–28, as described in CRC Report No. 259, "Road Rating Techniques," January 1951.

Example IX

To each of 2 samples of a gasoline containing 3.0 ml. of tetraethyllead per gallon and 15.2 ml. of isopropanol

per gallon as a solubilizing assistant and having a performance number of 108 in the mild test and 87 in the severe test, lithium 2-methyl-2-ethylbutyrate was added in quantities so that the blended gasoline contained 2.6 grams per gallon and 5.2 grams per gallon respectively. As a result, the performance numbers were raised to 115 and 128 respectively in the mild test and to 93 and 96 respectively in the severe test.

In Examples X to XVI inclusive the tests were carried out in an engine equipped with manifold fuel injection in accordance with the ASTM procedure indicated to show the knock resistance of fuels by the supercharge method. In these examples any performance number above 161, which is the presently official rating limit according to the ASTM test, was obtained by direct linear extrapolation, which is an accepted method.

Example X

To each of two samples of a commercial aviation gasoline containing 4.07 ml. of tetraethyllead per gallon and 76 ml. of isopropanol per gallon as a solubilizing assistant and having a performance number of 131 by the ASTM D–909–49T knock test method, lithium 1,2,2,3-tetramethylcyclopentane carboxylate was added in quantities so that the blended gasoline contained 0.85 gram per gallon and 3.4 grams per gallon respectively. As a result, the performance numbers were raised to 138 and 163 respectively in the ASTM D–909–49T knock test method.

Example XI

To each of two samples of a commercial aviation gasoline containing 4.6 ml. (7.8 grams) of tetraethyllead per gallon and 76 ml. of isopropanol per gallon as a solubilizing assistant and having a performance number of 139 by the ASTM D–909–49T knock test method, lithium 1,2,2,3-tetramethylcyclopentane carboxylate was added in quantities so that the blended gasoline contained 0.85 gram per gallon and 3.4 grams per gallon respectively. As a result, the performance numbers were raised to 148 and 168 respectively in the ASTM D–909–49T knock test method.

This same base gasoline containing 7 ml. (12 grams) of tetraethyllead gave a performance number of only 148 under the same test method.

Example XII

To each of two samples of a commercial aviation gasoline (no tetraethyllead) containing 76 ml. of isopropanol per gallon as a solubilizing assistant and having a performance number of 70 by the ASTM D–909–49T knock test method, lithium 1,2,2,3-tetramethylcyclopentane carboxylate was added in quantities so that the blended gasoline contained 0.85 gram per gallon and 12.0 grams per gallon respectively. As a result, the performance numbers were raised to 88 and 164 respectively in the ASTM D–909–49T knock test method. Concentrations of 1.70, 5.0 and 7.8 grams of this lithium compound per gallon raised the performance numbers to 107, 150 and 159 respectively. The gasoline of this example is the same as that employed in Example XI, except that it contained no tetraethyllead.

Example XIII

To each of three samples of isooctane was added ethanol and an ethanol solution containing 5.27 grams of lithium 2,2-dimethylpropionate per 100 ml. of ethanol in such quantities that the finished blends contained 76 ml. of ethanol per gallon and 0.53, 1.60 and 3.16 grams per gallon of the lithium compound respectively. As a result, the performance number of isooctane was raised from 100 to 137, 161 and 168 respectively in the ASTM D–909–49T knock test method. Even at concentrations of 0.05 gram of the lithium compound per gallon, a significant improvement in performance number is obtained.

Example XIV

To each of two samples of isooctane containing 1.5 ml. of tetraethyllead per gallon was added ethanol and an ethanol solution containing 5.27 grams of lithium 2,2-dimethylpropionate per 100 ml. of ethanol in such quantities that the finished blends contained 76.0 ml. of ethanol per gallon and 0.53 gram per gallon and 1.6 grams per gallon of the lithium compound respectively. As a result, the performance number of the leaded isooctane was raised from 133 to 159 and 168 respectively in the ASTM D–909–49T knock test method.

Example XV

To a sample of a commercial aviation gasoline containing 4.07 ml. of tetraethyllead per gallon and 190 ml. of ethanol per gallon as a solubilizing assistant and having a performance number of 131 by the ASTM D–909–49T knock test method, 1.6 grams of lithium 2,2-diethylhexanoate per gallon was added. As a result, the performance number was raised to 150 in the ASTM D–909–49T knock test method.

Example XVI

To an automotive gasoline which has a high aromatic content containing 3.0 ml. of tetraethyllead per gallon and 76 ml. of isopropanol per gallon and having a performance number of 125 by the ASTM D–909–49T knock test method, 5.0 grams of lithium 1,2,2,3-tetramethylcyclopentane carboxylate was added. As a result, the performance number was raised to 162. This same base gasoline containing 6.0 ml. of tetraethyllead (equivalent in weight to 3 ml. of tetraethyllead and 5.0 grams of this lithium compound) gave a performance number of only 137 in the same ASTM D–909–49T knock test method.

The amount of solvent used in the above examples to aid the solution of the lithium compounds does not materially affect the performance number of the fuel.

Example XVII

As previously mentioned, the antiknock activity of the compounds of this invention is not dependent upon the manner in which they are introduced into the combustion chamber of an engine. To illustrate this point, a lithium compound in the form of a dust was introduced into the intake air stream of an operating engine. The mild knock test procedure as described for Examples I to IX was employed, with the exception that the intake air temperature was 75° F. rather than 200° F., and the jacket cooling temperature was 300° F. rather than 212° F. As this test procedure did not readily lend itself to the determination of the actual performance numbers of the fuels, the knock resistance of these fuels is defined in terms of the highest useable knock-free compression ratio. It may be noted that under the mild test conditions an increase of one unit in the highest useable knock-free compression ratio is approximately equal to 20 performance numbers.

A sample of a gasoline containing 3.0 ml. of TEL per gallon had a highest useable knock-free compression ratio of 6.51 under the test conditions described in this example. When lithium 1,2,2,3-tetramethylcyclopentane carboxylate, in the form of a fine dust which had been passed through an 80-mesh screen, was added continuously to the intake air stream in a quantity sufficient to provide 2.70 grams of the lithium compound per gallon of gasoline, the highest useable knock-free compression ratio of this gasoline was increased to 6.77. A sample of the gasoline of this example containing a total of 4.0 ml. of tetraethyllead per gallon had a highest useable knock-free compression ratio of 6.78 under the test conditions of this example.

Example XVIII

The compounds of the present invention also show antiknock properties in fuels of the kerosene or JP–4 types (jet turbine fuel), which are useful in heavy duty spark ignition engines such as tractors, etc.

Using the engine under the severe test conditions outlined in the introduction to Example I, but with the fuel/air ratio of 0.19, intake air temperature of 300° F., manifold air pressure of 20 inches absolute, and using manifold fuel injection, a highly refined kerosene containing 3.0 ml. of tetraethyllead and 76 ml. of isopropanol per gallon was tested giving a performance number of 28 (29 octane number). When 6.8 grams of lithium 1,2,2,3-tetramethylcyclopentane carboxylate per gallon was added to this fuel, the performance number was raised to 31 (37 octane number). Under the same conditions, a JP–4 (commercial jet fuel) containing 3.0 ml. of tetraethyllead and 76 ml. of isopropanol per gallon was tested giving a performance number of 54. The addition of 6.8 grams of 1,2,2,3-tetramethylcyclopentane carboxylate per gallon raised the performance number to 59.

Example XIX

A method of preparation of the lithium salts of the tertiary carboxylic acids of this invention is exemplified with the 1,2,2,3-tetramethylcyclopentane carboxylic acid, and is accomplished by slurrying one mol of the acid in water and adding to this slurry an aqueous solution containing one mol of lithium hydroxide monohydrate. The mixture is agitated at room temperature until the acid dissolves, the solution is filtered, and the water is removed by drum drying. The salt is further dried in an oven at 100° C. Any of the lithium salts used in the present invention may be prepared in the same manner, using either the lithium hydroxide or other lithium base.

In general, however, the lithium compounds of tertiary 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 D–288–53 (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. However, as illustrated in Example XVIII, they are also useful in much lower quality fuels.

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, anticing agents; inhibitors for rust, corrosion, haze formation, gum formation; anti-preignition agents, etc.

The petroleum distillate 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 vary from 0.05 gram to 50 grams per gallon of fuel, the preferred range being between 0.5 to 20 grams 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 tertiary 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 employed in the specific examples above given, the lithium salts of other acids may be employed, such as: lithium 2-ethyl-2-n-butyldecanoate, lithium 2,2,3-trimethylbutanoate, lithium 2-methyl-2-ethylbutanoate, lithium 2,2,4,4-tetramethylpentanoate, lithium 1,3,3,4-tetramethylcyclopentane carboxylate, litium 1-methyl-3-isopropylcyclopentane carboxylate, lithium 1-n-butylcyclohexane carboxylate, lithium 1-cyclopentylcyclohexane carboxylate, lithium 2-methyl-2-cyclopentylpropionate, lithium 1-ethyl-4-(diethylmethyl)cyclohexene-2 carboxylate, and lithium 2-methyl-2-phenylpropionate.

In addition to the marked antiknock effect of the lithium salts of tertiary carboxylic acids, it has been found that the maximum knock-free power, as measured in the ASTM D–909-49T knock test method, occurred at a significantly leaner fuel/air ratio than that of the untreated fuels when these lithium compounds were employed to raise the performance number near or above the rating limit of the engine, which is 161 performance number.

A still further advantage of the use of the lithium salts of the present invention, particularly in aircraft engine operation, is the fact that they not only show marked antiknock effects under rich fuel/air ratio conditions, as measured by the ASTM D–909–49T knock test method, but also show marked antiknock activity at lean fuel/air ratios employed in normal cruising flight of aircraft.

What is claimed is:

1. A hydrocarbon fuel for spark ignition internal combustion engines, containing from 0.05 gram to 50 grams per gallon of a lithium salt of an organic tertiary carboxylic acid, the organic radical to which the carboxyl group is attached containing only carbon and hydrogen.

2. A hydrocarbon fuel for spark ignition internal combustion engines, containing from 0.5 gram to 20 grams per gallon of a lithium salt of an organic tertiary carboxylic acid, the organic radical to which the carboxyl group is attached containing only carbon and hydrogen.

3. A hydrocarbon fuel for spark ignition internal combustion engines, containing from 0.05 gram to 50 grams per gallon of the lithium salt of 1,2,2,3-tetramethylcyclopentane carboxylic acid.

4. A hydrocarbon fuel for spark ignition internal combustion engines, containing from 0.05 gram to 50 grams per gallon of the lithium salt of 2,2-dimethylpropionic acid.

5. In the method of operating a spark ignition internal combustion engine in which the fuel is introduced into the combustion chambers of the cylinders under subatmospheric to superatmospheric pressures, the step which comprises introducing into the combustion chamber so that it is present at the time the fuel is ignited, a lithium salt of an organic tertiary carboxylic acid, the organic

radical to which the carboxyl group is attached containing only carbon and hydrogen, at the rate of from 0.05 gram to 50 grams per gallon of fuel.

6. In the method of operating a spark ignition internal combustion engine in which the fuel is introduced into the combustion chambers of the cylinders under subatmospheric to superatmospheric pressures, the step which comprises introducing into the combustion chamber so that it is present at the time the fuel is ignited, a lithium salt of an organic tertiary carboxylic acid, the organic radical to which the carboxyl group is attached containing only carbon and hydrogen, at the rate of from 0.5 gram to 20 grams per gallon of fuel.

7. A hydrocarbon fuel for internal combustion engines containing up to 6.0 ml. of tetraethyl lead and from about 0.05 gram to about 50 grams per gallon of a lithium salt of an organic tertiary carboxylic acid, the organic radical to which the carboxyl group is attached containing only carbon and hydrogen.

8. A hydrocarbon fuel for internal combustion engines containing up to 6.0 ml. of tetraethyl lead and from 0.5 gram to 20 grams per gallon of a lithium salt of an organic tertiary carboxylic acid, the organic radical to which the carboxyl group is attached containing only carbon and hydrogen.

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