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HYDROCARBON-SOLUBLE ALKALI METAL COMPOSITIONS

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This invention relates to new chemical compositions, and particularly to new and valuable hydrocarbon fuels for spark-ignited internal combustion engines. The present invention is particularly directed to a method for putting in solution in liquid hydrocarbons lithium salts of branched chain carboxylic acids.

It has been found that the lithium salts of branched chain carboxylic acids improve the antiknock characteristics of gasolines. Their use, however, is restricted to some extent because of their limited solubility in gasolines, While the solubility of these lithium salts in gasolines can be improved by the addition of such solvents as alcohol, such mixtures are not entirely satisfactory because of the large amount of alcohol which must be employed to produce even relatively low concentrations of the salt in the hydrocarbon fuel.

It is an object of the present invention to provide compositions of lithium salts of aliphatic branched chain carboxylic acids which are readily soluble in liquid hydrocarbons, which compositions as such, or as concentrates in liquid hydrocarbon media, are useful as antiknock agent for gasolines.

According to the present invention, the amount of the lithium salts of branched chain carboxylic acids that can be dissolved in liquid hydrocarbons can be materially increased by incorporating therewith a hydrocarbon-soluble, branched chain carboxylic acid. The molar ratio of the acid to the lithium salt will ordinarily be within the range of from 10:1 to 0.5:1. By this method it has been found that sufficient lithium salts can be put in solution in liquid hydrocarbons so as to provide at least about 0.0025 gram of lithium per liter of solution. The ratio of acid to salt can be decreased even below the 0.5:1 where relatively small additions of other solvents such as alcohol are employed.

The lithium salts of aliphatic branched chain carboxylic acids with which the present invention is involved are those containing from 4 to 30 carbon atoms and which have at least one open chain branch attached to one of the first six carbon atoms in the molecule. Since the branchings on the chain may join to form a cycloaliphatic ring, the term "aliphatic branched chain" is meant to include cycloaliphatic and also the aliphatic-cycloaliphatic types. These branched chain aliphatic carboxylic acids may also have aromatic rings attached to the carbon chains. The free acids used as solubilizing agents are of the same class as those used in making the lithium salts.

Representative acids of this class from which the lithium salts may be derived and which as free acids may be used as solubillizing agents for the lithium salts, are: isobutyric (2-methylpropanoic), pivalic (2,2-dimethylpropanoic), 2-methylbutanoic, isovaleric (3-methylbutanoic), 2-ethylbutanoic, 2,2-dimethylbutanoic, 2,3-dimethylbutanoic, 3,3 - dimethylbutanoic (t - butylacetic), isocaproic (4-methylpentanoic), 2,2-dimethylpentanoic, 2,3-dimethylpentanoic, 2-ethyl-2-methylbutanoic, 4,5-dimethylhexanoic, 2-ethylhexanoic, 2,2,4,4-tetramethylpentanoic, 3,5,5-trimethylhexanoic, 2-ethyl-4,4-dimethylpentanoic 4-ethyl-5,5-dimethylhexanoic, 2,2-diethylhexanoic, 2 - propyl - 4 - methylpentanoic, 2 - isopropyl - 5 - methylhexanoic, 2-heptylnonanoic, 2-hexyldecanoic, 2-ethyl-2-butyldecanoic, 2,2-dimethyldodecanoic, 2,2-dimethylhexadecanoic, 2,2-dimethyloctadecanoic, campholic acid (1,-2,2,3-tetramethylcyclopentane-1-carboxylic acid), isofencholic acid, 3-methyl-3-cyclohexylbutanoic, 3,3,4-trimethylcyclopentylacetic, 1,4 - diisopropylcyclohexane - 1 - carboxylic acid, 1-ethyl-4(bis-ethylmethyl)cyclohex-2-ene-1-carboxylic acid, 1-methyl-2,5-endomethylene-cyclohexane-1-carboxylic acid, 3-ethylpent-2-enoic, and 3-ethylpent-3-enoic acid.

Either the same acid used in making the lithium salt or a different acid of the class may be used to increase the solubility of the salt in hydrocarbon fuels. A different acid is preferred, since increased solubility is usually obtained. It is of course understood that mixtures of acids can be used to increase the solubility of a single salt or mixtures of salts.

The acid-salt compositions of the present invention may be prepared simply by mixing a lithium carboxylate and a carboxylic acid of the class defined. The components may be mechanically mixed, or fused by heating, or they may be brought together in a solvent. If the solvent is a low-boiling alcohol or benzene, it is readily removed from the acid-salt mixture and the mixture recovered by distilling off the solvent. Alternately, the acid may be partially neutralized to the desired extent by the addition thereto of a suitable lithium base. Similarly, the acid-salt composition may be prepared in a volatile liquid hydrocarbon, which hydrocarbon may or may not be removed as desired; thus, the compositions may be prepared in situ in liquid hydrocarbon media which may serve as a carrier, e.g. benzene, toluene, heptane, isooctane, diisobutylene, kerosene, gasoline, and mixtures thereof. When a lithium alcoholate is used as such or as a concentrated alcoholic solution, the alcohol introduced and formed in the neutralization reaction may or may not be removed, as desired.

The acid-salt compositions themselves at ordinary temperatures may vary from relatively fluid or viscous liquids through semi-solids to solids, depending upon the chemical structure and physical properties of the particular acids employed in their preparation and upon the acid/salt mol ratio.

The acid-salt compositions of this invention are adapted to provide practical working concentrations of dissolved lithium in media consisting essentially of liquid hydrocarbons. The hydrocarbon may constitute the major component of the solution or a relatively minor component of the solution, such as when they are dissolved in the hydrocarbon fuel itself or when made up as concentrates for addition to fuels either in a hydrocarbon or when the salt is dissolved in the acid itself, as illustrated in the following examples.

The particular liquid hydrocarbon medium employed in the preparation of concentrates for addition to fuels is not critical. It may be a single hydrocarbon or a mixture of such hydrocarbons such as paraffinic, isoparaffinic, olefinic, naphthenic or aromatic, or blends thereof. The acid-salt mixtures may also be incorporated as concentrates in other gasoline additives such as in the tetraethyllead antiknock compounds. The fuels with which the lithium salts of this invention are to be used are the liquid hydrocarbon fuels which comprise the various gasolines of commerce used in spark-ignition engines. Such fuel may be a clear stock, i.e. not containing additives, or it may be a finished commercial fuel containing additives normally associated with such fuels, e.g. antioxidants, corrosion inhibitors, anti-icing agents, antiknocks, scavenging agents for combustion products of such antiknocks, etc. By the term "leaded fuel" as used herein is meant a fuel containing an antiknock quantity of tetraethyllead, e.g. 0.12 to 1.5 ml. per liter, and the appropriate quantities of halohydrocarbon scavengers for lead, e.g. ethylene dibromide, ethylene dichloride and the like.

These acid-salt compositions are effective antiknock agents, and when so employed will be present in quantities providing from about 0.0025 to about 1.5 grams, and preferably 0.05 to 0.5 gram of lithium per liter. By the use of acids, concentrations of lithium as lithium salts in the hydrocarbon solvents even up to about 20 grams per liter have been obtained.

The ratio of acid to salt employed will usually vary depending upon the concentration of the lithium desired in the final fuel. As stated above, the acid/salt ratio will also vary depending upon the chemical structure of the acids and salts used. Usually the acid/salt ratio will be greater as the concentration of such mixture in the hydrocarbon fuel decreases. The acid-salt concentration to be employed in the final fuel mixture will dictate the ratio of the acid-salt mixture in the concentrate made up for addition to fuels.

It has also been found that the presence of small amounts of a lower molecular weight alcohol or other solvent such as dimethylformamide, will substantially lower the amount of acid required to effect complete solution of the lithium carboxylate in the hydrocarbon fuel. The amount of the alcohol or dimethylformamide employed usually will not be more than 0.25 to 1.0 volume percent, based on the hydrocarbon fuel, although larger amounts may be employed if desired. In fuels already containing alcohol or dimethylformamide as a de-icing agent, the ratio of acid to salt may be somewhat lower than that used in a hydrocarbon fuel alone, not containing such agents.

The presence of the acid solubilizing component in the acid-salt compositions of this invention has no deleterious effect on the performance of the liquid hydrocarbon fuels. Usually it exerts the beneficial effect of augmenting the antinock performance of the lithium carboxylate. Further, the acid-salt compositions provide the additional advantage of being markedly more resistant to extraction by water from its hydrocarbon solutions than is the salt itself.

In the examples, the solubilities were determined after centrifuging the solutions at 2700 r.p.m. for 15 minutes to throw out any undissolved material.

The following examples are given to illustrate the invention.

EXAMPLE 1

The solubilizing effect of each of seven branched chain acids was determined by adding 0.1 gram of lithium pivalate to 100 ml. of a commercial aviation gasoline in which the pivalate was substantially insoluble. To the resulting suspension was added approximately an equal molar quantity of the branched chain carboxylic acid, and the mixture was mechanically shaken at room temperatures. After one hour, if a solid phase still remained, the addition of acid was repeated, i.e. a second molar equivalent and then a third, etc., as needed, to effect complete solution of the solid phase. The quantity of each acid required is tabulated below:

Acid	Amount required for solubilization	
	Grams	Acid/salt ratio
2,2-dimethylbutanoic	0.12	1.1:1
2-ethyl-2-methylbutanoic	0.13	1.1:1
3,5,5-trimethylhexanoic	0.16	1.1:1
Isofencholic	0.17	1.1:1
2,2,4,4-tetramethylpentanoic	0.32	2.2:1
Campholic	0.34	2.2:1
Pivalic (2,2-dimethylpropanoic)	0.50	5.0:1
2-hexyldecanoic	0.79	3.2:1

Substantially identical results were obtained in the above gasoline which had been treated with commercial tetraethyllead aviation mix to contain approximately 1 ml. of tetraethyllead per liter.

The solutions produced above are stable indefinitely, that is, they remain clear and form no precipitate of lithium salts.

EXAMPLE 2

According to the procedure described in Example 1, approximately 0.1 gram of each of the lithium salts listed below was completely solubilized in 100 ml. of isoctane, by the addition thereof of a carboxylic acid as designated below:

Lithium Salt	Grams	Carboxylic acid	Solution	
			Concen. lithium grams/liter	Acid/salt ratio
2-methyl-propanoate.	0.1	2,2-dimethyl propanoic.	0.07	6:1
2,2-dimethyloctadecanoate.	0.1	2,2-dimethyloctadecanoic.	0.02	2:1
2,2-dimethyloctadecanoate.	0.1	2,2-dimethylbutanoic.	0.02	5.5:1
2-ethylhexanoate	[1] 0.15	2-methylpropanoic	0.06	4:1
2-ethylhexanoate	0.125	2-ethylhexanoic	0.06	4:1
2-ethylhexanoate	0.125	Pivalic	0.06	1.6:1
Pivalate	0.09	2-ethylhexanoic	0.06	1.6:1

[1] In 100 ml. of a leaded (0.8 ml. tetraethyllead/liter) automotive gasoline.

EXAMPLE 3

Using kerosene in the procedure described in Example 1, 4 grams of 2-ethylhexanoic acid solubilized 1 gram of lithium-2-ethylhexanoate per liter of kerosene; and using JP–4 jet fuel as the solvent, one gram of the salt was solubilized by 6 grams of the acid per liter of solvent.

EXAMPLE 4

Each of the following lithium carboxylates together with about 3.2 molar proportions of its corresponding carboxylic acid was blended into isoctane by stirring at room temperatures:

2-methyl-2-ethylbutanoate
2,2,4,4-tetramethylpentanoate
3,5,5-trimethylhexanoate
2-ethylhexanoate
2-hexyldecanoate
Campholate
Isofencholate

In each case the quantity of salt was sufficient to provide 0.066 gram of lithium per liter of isooctane. The resulting acid/salt/isoctane compositions were clear liquids.

Substantially identical results are obtained on employing leaded and unleaded commercial automotive and aviation gasolines.

In control tests, in which the carboxylic acid component was excluded, the lithium salts were substantially insoluble.

EXAMPLE 5

A solution of 0.185 gram of 2-methylbutanoic acid in 100 ml. of isoctane was stirred at room temperature with an excess of lithium 2-methylbutanoate (which is normally insoluble) until the solution was saturated with respect to dissolved lithium salt. The isoctane phase contained all of its original acid content and 0.045 gram of lithium 2-methylbutanoate: acid/salt ratio=4.3:1.

When the above experiment was repeated with isoctane containing 1.85 grams of the 2-methylbutanoic acid, 1.46 grams of the lithium salt dissolved: acid/salt ratio=1.4:1.

EXAMPLE 6

The procedure of Example 5 was repeated, employing each of the following acids and the corresponding lithium salts thereof, in 100 ml. portions of isoctane:

0.1 gram of 2-hexyldecanoic acid solubilized 0.04 gram of lithium 2-hexyldecanoate; acid/salt ratio=2.5:1;

0.5 gram of 3-methylbutanoic acid solubilized 0.26 gram

of its lithium salt; acid/salt ratio=approximately 2:1;
2.0 grams of 2-ethylbutanoic acid solubilized 0.67 gram of its lithium salt; acid/salt ratio=about 3:1; and
26 grams of 3,5,5-trimethylhexanoic acid solubilized 18.2 grams of its lithium salt; acid/salt ratio=about 1.5:1.

EXAMPLE 7

Campholic acid, lithium campholate, and the following hydrocarbon solvents were employed in the procedure of Example 5. The results are tabulated below:

Solvent (100 ml.)	Acid, grams in soln.	Salt, grams solubilized	Lithium, grams/liter
n-Heptane	0.36	0.37	0.15
Do	10	13.4	5.3
Cyclohexane	2	2	0.8
Isooctane	0.02	0.03	0.012
Do	0.2	0.26	0.1
Do	1.0	1.4	0.55
Do	10	14	5.5
Diisobutylene	10	10	4.0

EXAMPLE 8

The solutions described in the table below were prepared from 2-ethylhexanoic acid, lithium 2-ethylhexanoate and isooctane, by the procedure given in Example 5. As shown, the quantities of both the acid and the salt are expressed in grams per liter of total solution. It should be noted that solution 7, a viscous liquid, was prepared in the absence of isooctane, by mixing with stirring 0.82 gram of lithium 2-ethylhexanoate per gram of 2-ethylhexanoic acid.

Lithium 2-ethylhexanoate/2-ethylhexanoic acid/isooctane solutions (grams/liter)

Solution	Acid	Salt	Lithium	Acid/salt Molar ratio
1	0.5	0.006	0.003	8.8
2	2.0	0.7	0.03	3.0
3	22.3	15.2	0.71	1.5
4	40.0	30.0	1.4	1.4
5	193	158	7.3	1.27
6	435	357	16.6	1.27
7	[1] 516	[1] 427	[1] 19.6	[1] 1.27

[1] No isooctane present.

EXAMPLE 9

A mixture consisting of 30 grams of isofencholic acid and 29 grams of lithium isofencholate was completely soluble in 100 ml. of isooctane at 27° C. In contrast, the solubility of lithium isofencholate alone in isooctane is less than 0.003 gram per liter.

An equimolar mixture of isofencholic acid and lithium isofencholate, containing 18.2 grams of the salt, was stirred into 100 ml. of isooctane. The resulting solution was diluted with isooctane to ⅕, 1/10, 1/20, then 1/40 volume, without the separation of a solid phase occurring.

EXAMPLE 10

2,2-dimethyloctadecanoate was slurried in isooctane in quantity corresponding to 20 grams of salt and 0.44 gram of lithium per liter, followed by an equal weight, based on the salt, of 2,2-dimethyloctadecanoic acid. The mixture was stirred to produce a clear solution.

In the following examples, the "mild" knock test was carried out 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 condition mild
Speed, r.p.m.	600
Spark advance (degree before top center)	13
Fuel injection timing (degree after top center on intake stroke)	50
Fuel/air ratio	0.0800±0.0005
Intake manifold air pressure (in. Hg abs.)	30
Coolant temperature, ° F	212
Intake temperature, ° F	200
Oil temperature, ° F	160

Compression ratio—Varied to produce trade 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. The knock resistance of all fuels tested is expressed in this specification in terms of Army-Navy Performance Numbers (U.S.A.) 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.

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

EXAMPLE 11

A leaded blended gasoline, having a composition typical of a commercial automotive gasoline and containing 0.8 ml. of tetraethyllead per liter, was treated to contain 0.066 gram of lithium per liter by dissolving in the gasoline a 3:1 molar ratio mixture of 2-ethylhexanoic acid and lithium 2-ethylhexanoate, in quantity providing 4.5 grams of the acid and 1.4 grams of the lithium salt per liter of fuel.

As determined in the "mild" knock test method, the performance number of the untreated fuel was 104; that of the treated fuel was 131.

EXAMPLE 12

A mixture consisting of 1.3 mols of pivalic acid per mol of lithium 2-ethylhexanoate was dissolved, in quantity providing 0.066 gram of lithium per liter, in the gasoline of Example 11. As a result, the performance number of the fuel was raised from 104 to 133 in the "mild" test.

EXAMPLE 13

The gasoline of Example 11 was treated to contain 0.066 gram of lithium per liter by dissolving therein 8.7 grams per liter of a 2.5:1 molar mixture of 3-hexyldecanoic acid (6.2 grams) and lithium 2-hexyldecanoate (2.5 grams). The performance number of the gasoline was raised thereby from 104 to 115 in the "mild" test. Only 6% of the lithium salt present in this solution was extracted with 5 ml. of water per 100 ml. of the gasoline solution, while when the same quantity of salt is solubilized in gasoline using 55 g. per liter of ethanol, the same amount of water extracted 96% of the salt from the solution.

EXAMPLE 14

By the use of the blending agents tabulated below, lithium 3,3-dimethylbutanoate, in quantity providing 1.2 grams per liter of additive (0.066 gram per liter of lith-

ium) was dissolved in a super-premium leaded automotive gasoline having a performance number (P.N.) of 105 in the "mild" test. As a result, the P.N. of the fuel was raised as indicated below:

Blending agent	P.N.	Increase in PN
40 grams/liter of ethanol	115	10
1.4 grams/liter of pivalic acid	131	26
1.9 grams/liter of 2-ethylhexanoic acid	129	24

EXAMPLE 15

The previous example was repeated, employing the lithium carboxylates and carboxylic acids tabulated below. The quantities are in grams per liter, unless otherwise noted.

Grams	Lithium Carboxylate	Grams	Solubilizer	Increase in P.N.
1.4	Lithium triethylacetate.	40	Ethanol	9
1.4	do	1.4	Pivalic acid	9
1.4	do	1.9	2-ethylhexanoic	9
1.4	Lithium 2-ethyl-4-methyl pentanoate.	40	Ethanol	7
1.4	do	1.9	2-ethyl-4-methyl pentanoic acid.	10
1.4	Lithium 2-ethylhexanoate.	1.9	2-ethylhexanoic	18
1.4	do	1.4	Pivalic acid	15
1.05	Lithium pivalate	1.9	2-ethylhexanoic	10

EXAMPLE 16

A 2:1 molar mixture of pivalic acid and lithium pivalate, in an amount providing 0.05 gram of lithium per liter, was dissolved in a premium unleaded automotive gasoline having a performance number of about 91 in the "mild" test.

As a result, the performance number of the fuel was raised to 108.

EXAMPLE 17

A 1:1 molar mixture of campholic acid and lithium campholate was dissolved, in amounts provided 0.034 gram and 0.069 gram of lithium per liter of fuel, in a blended gasoline containing 0.8 ml. of tetraethyllead per liter and having a performance number of 116 in the "mild" test and 86 in the "aviation" test, which was carried out by the procedure set forth in ASTM D-909-49T knock test method. As a result, the performance number of the fuel was raised to 126 and 140, respectively, in the "mild" test and to 98 and 103, respectively, in the "aviation" test.

The embodiments of the invention in which an inclusive property or privilege is claimed, are defined as follows:

1. A liquid hydrocarbon fuel for internal combustion engines containing as an antiknock agent a lithium salt of an aliphatic branched chain carboxylic acid, the amount of the lithium salt of the aliphatic branched chain carboxylic acid being increased over its normal solubility in such liquid hydrocarbon by having incorporated therewith an aliphatic branched chain carboxylic acid, the carboxylic acids and the carboxylic acid salts being those in which the carboxy group is attached to a hydrocarbon radical, the molar ratio of acid to salt in the composition being within the range of from about 10:1 to 0.5:1.

2. A liquid hydrocarbon containing dissolved therein at least 0.0025 gram/liter of lithium as a lithium salt of an aliphatic branched chain carboxylic acid in which the solubility of the salt in the liquid hydrocarbon has been effected by incorporating in the hydrocarbon from 0.5 to 10 mols of an aliphatic branched chain carboxylic acid per mol of said salt, the carboxylic acids and the carboxylic acid salts being those in which the carboxy group is attached to a hydrocarbon radical.

3. A method for improving the solubility of lithium salts of aliphatic branched chain carboxylic acids in liquid hydrocarbons, which comprises incorporating in the hydrocarbon solution from 0.5 to 10.0 mols of an aliphatic branched chain carboxylic acid per mol of salt present, the carboxylic acids and the carboxylic acid salts being those in which the carboxy group is attached to a hydrocarbon radical.

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