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3,563,715

MOTOR FUELS

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No Drawing. Filed July 15, 1958, Ser. No. 748,624

Int. Cl. C101 1/18

U.S. Cl. 44—66

23 Claims

The present invention relates to leaded high-octane hydrocarbon fuels for spark-ignition internal combustion engines, the octane rating of which the fuels is further enhanced by the introduction into these fuels of certain monocarboxylic acids and/or materials capable of providing such acids immediately prior to the combustion of these fuels. More particularly, it relates to leaded high-octane gasolines improved by the introduction into these gasolines of said monocarboxylic acids, and/or materials capable of providing such acids immediately prior to the combustion of gasoline in amounts effectively increasing the octane rating and, consequently, the anti-knock quality of the gasoline.

The octane numbers of motor gasolines have risen steadily through the years in order to keep pace with the increase in compression ratios of automobile and aviation engines, the increase being the result of a continuing demand for more engine power and better engine performance. Accordingly, by resorting to a variety of refining processes and blending techniques, the petroleum industry is now able to supply commercial gasolines with octane numbers of the order of 90 and above. Nevertheless, compression ratios continue in their upward trend and, in these circumstances, it is found that addition to the high-octane gasolines of organo-metallic anti-knock additives, particularly of lead alkyls, such as tetraethyl lead, conventionally added in amounts of the order of 3 cc. per gallon, cannot provide the desired freedom from knock when these gasolines are used in engines operating at compression ratios above 9:1, and thus again a further increase in octane numbers is required for knock-free operation. A further increase of the octane rating, however, by additional refining treatments of gasoline fractions becomes increasingly costly and difficult. At the same time, addition of lead-containing anti-knock additives, such as tetraethyl lead, in amounts above the conventional maximum of 3 cc. per gallon of gasoline, is not economically attractive, since the cost increment incurred by the introduction of additional lead is not compensated by a corresponding octane number increase of sufficient magnitude.

It has now been found that the knock-suppressing action of lead alkyl anti-knock additives, and, in particular, of tetraethyl lead, can be advantageously and significantly enhanced in high-octane gasolines by the introduction into these gasolines of certain organic materials in amounts which, although small, are capable of extending appreciably the anti-knock action of the lead alkyl additive, such as tetraethyl lead. These organic materials will be referred to hereinafter in this specification as anti-knock synergists or lead extenders.

Generically defined, the organic material operative as anti-knock synergists in high octane leaded gasolines are either gasoline-dispersible monocarboxylic acids thermally stable up to about 200° C., or gasoline-dispersible organic compounds which, by their thermal decomposition in the combustion chamber, provide therein similar free monocarboxylic acids thermally stable at about 200° C., effective in enhancing (extending) the anti-knock property of the lead alkyl additive to the gasoline.

The exact mechanism underlying the action of the free monocarboxylic acid in the combustion chamber is not completely understood, but it is conjectured that,

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under the circumstances existing in the combustion chamber, it tends somehow to prolong the life of the anti-knock "lead species" formed in the decomposition of the lead alkyl additive. Accordingly, it is important that the monocarboxylic acid, or the compound capable of providing the same, arrive in the combustion chamber undecomposed and preferably exist therein as a free monocarboxylic acid through the stage of preflame oxidation.

Whether or not the beneficial effect of the presence of a free monocarboxylic acid occurs in the preflame oxidation stage during the induction period, and whether or not the free monocarboxylic acid actually reacts with the lead alkyl component is not known.

Monocarboxylic acids which are thermally stable, i.e., are capable of existing as a free acid, at temperatures up to about 200° C., represent effective lead extenders. By the same token, materials providing such acids on being introduced with the gasoline into the combustion chamber likewise represent satisfactory lead extenders.

In any event, whatever be the true mechanism, the presence of a free monocarboxylic acid in the fuel-air mixture, whether by virtue of incorporation as such in the gasoline or by being liberated in the combustion chamber from a given suitable material, a real and appreciable increase in octane rating of leaded gasoline is achieved. This increase is reflected in the elimination or at least in a substantial reduction of the knock phenomenon, and hence in a better engine performance, despite the application of high compression ratios.

The very designation of the additives of this invention as "lead extenders" indicates that they are to be used in "leaded" gasolines, that is, in gasolines containing lead alkyls as anti-knock agents, and, in particular, in those containing tetraethyl lead. When the small quantities of the organic materials, which in leaded gasolines provide a free monocarboxylic acid in the combustion chamber of a spark-ignition engine and improve thereby the knock behavior of these gasolines, are added to an "unleaded" gasoline, the effect on the octane rating of this latter is essentially nil. The terminology "leaded gasoline," as employed in this specification, refers in general to the petroleum fraction boiling in the gasoline hydrocarbon range (e.g., from about 10 to about 230° C.), to which there has been added a small amount from about 0.5 to about 6 cc. per gallon, and even more, of a lead alkyl anti-knock compound, as exemplified by tetraethyl lead (TEL), tetraisopropyl lead, diisopropyl diethyl lead, tetramethyl lead and the like. The designation TEL is the abbreviation commonly accepted in the trade for tetraethyl lead which is the preferred and at the present time almost universally employed anti-knock additive to automobile and aviation gasolines; and which may be employed either with or without conventional halogen scavengers, such as ethylene bromide, ethylene chloride, and the like.

Petroleum fractions boiling in the gasoline range may consist of straight-chain and branched-chain paraffins, olefins, aromatics (mainly alkyl aromatics) and naphthenes. Presently, gasolines supplied to the trade as motor fuels represent a variety of mixtures and blends of these different hydrocarbons. As a rule, the content of straight-chain paraffins in such gasolines is kept as low as possible, since these "normal" paraffins are known for their tendency to knock. The content of naphthenes (cycloparaffins) in a modern high-octane gasoline is generally quite low, owing to the extensive refining and reforming treatments used to convert the bulk of naphthenes to aromatics characterized by higher octane numbers. Consequently, modern commercial gasolines by and large represent mixtures or blends of aromatics, branched-chain paraffins and olefins with but minor contents of cycloparaffins and knock-prone straight-chain paraffins.

Addition of the organic materials, which provide a free monocarboxylic acid in accordance with the invention, to any of these gasolines containing a lead alkyl anti-knock additive, whether isoparaflinic (branched-chain), olefinic, aromatic or cycloparaflinic (naphthenic), will enhance the octane rating above a certain minimum initial Research octane number which varies depending on the particular composition and the structure of hydrocarbons in gasoline.

A particular feature of the invention is that the availability of the aforementioned free monocarboxylic acids in the combustion chamber will not afford enhanced octane ratings even for a leaded gasoline, unless the original "Research" octane number of this latter, as determined prior to the addition of the synergist or lead extender by the known CFR engine method, is above a certain critical minimum value which in all events lies at about 90 and above.

The lead extenders of the invention have been extensively tested in various leaded gasolines which included in their number gasolines prepared from essentially the same kind of hydrocarbons, e.g., aromatics, olefins, and branched-chain paraffins, gasolines representing mixtures in different proportions of two, three and more different kinds of hydrocarbons, for instance, blends of aromatics and branched-chain paraffins, mixtures of aromatics, olefins and branched-chain paraffins, etc. Both in the extensive laboratory tests (amounting to several thousand runs), using CFR Research and ASTM Motor methods, and in equally extensive series of road octane number determinations, these lead extenders provided a significant improvement of the octane value in leaded gasolines of a minimum Research octane number of at least about 90.

This improvement was observed in the runs made with essentially (from 90 to 100% by volume) aromatic and olefinic gasolines. Gasolines which consisted of two, or three, or more kinds of hydrocarbons boiling in the gasoline range, of which at least 5% by volume was made up of aromatics or olefins, were likewise improved with respect to their octane rating by the addition of the lead extenders of the invention. Thus, as it will be seen from the illustrative data shown further on in this description, the octane rating of leaded gasolines with a paraflinic (cyclo- and branched-chain) hydrocarbon content up to 95% by volume can be significantly enhanced by the addition thereto of the lead extenders. In essentially (95-100% by volume) cycloparaflinic gasolines, however, the addition of the lead extenders becomes apparent when the original minimum Research octane number thereof is about 95 or higher, while in essentially branched-chain paraflinic gasolines the original minimum octane number should lie at about 105 before an increment of the octane value is obtained upon the addition of the lead extenders.

Mixed leaded aromatic-branched-chain paraflinic and aromatic-branched-chain paraflinic-olefinic gasolines with initial Research octane numbers of at least about 90, which may also contain some cycloparaflins (up to 15-20% by volume), are presently made available on the market for consumer use and represent particularly suitable gasolines for the purpose of improving their knock resistance by the incorporation of the lead extenders in accordance with the invention.

While the effectiveness of all lead alkyl compounds capable of improving the knock-resistance of gasolines, e.g., tetrapropyl lead, diisopropyl diethyl lead, tetramethyl lead, and the like, can be enhanced by the addition thereto of the lead extenders of this invention, since tetraethyl lead (TEL), at least up to the present time, constitutes the generally preferred lead alkyl anti-knock additive to gasoline, in the following description all references to the lead additive are references to TEL employed in the conventional amount of 3 cc. per gallon of gasoline, unless otherwise specified.

As stated hereinbefore, the anti-knock synergists or lead

extenders of the invention, which provide in the combustion chamber a free monocarboxylic acid and thus enhance the anti-knock property of the lead alkyl additive to the gasoline are to be employed in relatively small though effective proportions which bear a critical ratio to the amount of lead in the gasoline. These proportions range from about 3 to about 60 moles of the extender per each gram-atom of the lead in the gasoline. The effect of the extender is particularly satisfactory when it is present in the gasoline in amounts from about 5 to about 30 moles per each gram-atom of lead.

The lead extenders of the invention should be dispersible in gasoline and, in addition, they should be unreactive with the lead alkyl present therein at temperatures up to about 40° C. When introduced with gasoline, and in concentrations from about 3 to about 60 moles per each gram-atom of the lead, into the combustion chamber of a running spark-ignition engine, they supply a free monocarboxylic acid in that chamber. Provided this free acid is not of the kind which tends to form metal chelates, its presence in the combustion chamber results in an enhancement of the anti-knock action of the lead alkyl additive, and, correspondingly, in an increment of the octane rating of the gasoline.

It was also found that, in order to achieve this improvement of the octane rating, and thus to decrease knocking of high-octane leaded gasoline, the monocarboxylic acids to be provided in the combustion chamber in accordance with the invention by the lead extender materials dispersed in the gasoline should not contain sulfur, chlorine or bromine in their molecular structure.

Henceforth, the broad class of lead extenders of the invention can be separated into two subdivisions:

(A) Gasoline-dispersible monocarboxylic acids characterized by the absence of sulfur, chlorine or bromine and unreactive with lead alkyls at temperatures up to about 40° C. In practical terms, this means that the acids are unreactive with lead alkyls at room temperature, because the actual time between the passage of the gasoline containing the lead extender in the form of a free monocarboxylic acid into the combustion chamber is so short that, even though the acid could perchance react with the lead alkyl at temperatures above about 40° C., prior to entering the combustion chamber, it would not actually have time to do so. Furthermore, these monocarboxylic acids should not be of the kind which form metal chelates and should be thermally stable up to about 200° C. and preferably should remain stable through the stage of pre-flame oxidation in the combustion chamber.

(B) Gasoline-dispersible organic materials, devoid of sulfur, chlorine and bromine, unreactive with lead alkyls at temperatures up to about 40° C., and, under the temperature conditions obtainable in the combustion chamber, providing or releasing therein a free monocarboxylic acid falling within the definition of effective acids of the above subdivision (A). Consequently, the acids thus released by these organic materials of subdivision (B) in the combustion chamber should be similarly of the kind which do not form chelated rings with metals and are thermally stable at about 200° C. and at temperatures incidental to the stage of pre-flame oxidation in the combustion chamber.

Whether classifiable under subdivision (A) or under subdivision (B), the lead extenders of this invention are to be free of any substituents which may counteract or interfere with their beneficial effect on the anti-knock behavior of leaded gasoline. On the other hand, the presence of many a substituent in a monocarboxylic acid, or in an organic material capable of providing such acid in the combustion chamber according to the invention, not only has no adverse effect on its action as a lead extender for gasoline but often is responsible for additional beneficial properties.

As illustrative examples of organic materials containing substituents and, nevertheless, operative in accordance with the invention, there may be mentioned alkoxy-sub-

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stituted hydrocarbon-type monocarboxylic acids, e.g., methoxyacetic acid, and esters of dicarboxylic aliphatic acids having one completely esterified carboxyl group, e.g., ethyl acid adipate, which actually function as free stable monocarboxylic acids and extend the anti-knock effect of the lead in gasoline.

Of course, any of the monocarboxylic acids operative in accordance with the invention may be introduced into the combustion chamber in the form of esters, amine salts, acid anhydrides and other organic materials dispersible in gasoline, which release such monocarboxylic acids in the combustion chamber of a running spark-ignition engine.

Both gasoline-dispersible hydrocarbon monocarboxylic acids of the general formula RCOOH , wherein R is a hydrocarbon radical, and gasoline-dispersible organic materials which produce or liberate in the combustion chamber such hydrocarbon monocarboxylic acids represent materials suitable for use as additives to leaded gasolines in accordance with the invention. The hydrocarbon portion R of the foregoing general formula may be any organic radical entirely consisting of carbon and hydrogen atoms, for instance, a straight-chain alkyl, a branched-chain alkyl, a cycloalkyl, an aryl, an alkenyl, an alkynyl, an alkyl aryl, an aralkyl, etc., radical. Generally, any hydrocarbon monocarboxylic acid containing at least two carbon atoms and dispersible in gasoline in such proportions that the mole ratio thereof to the lead in the gasoline may lie between 3:1 to 60:1 can be effectively employed as a lead extender. To illustrate: in the fatty acid (alkane) series, any gasoline-dispersible acid from acetic to lignoceric and even higher may be employed.

Aromatic acids, e.g., benzoic and naphthoic, the several toluic acids, xylic acids, and the like, are also effective as lead extenders.

Unsaturated hydrocarbon monocarboxylic acids, namely, mono-olefin (alkene) monocarboxylic acids, such as β,β -dimethylacrylic acid, or materials which provide these acids in the combustion chamber, and monoacetylene (alkyne) monocarboxylic acids as well as materials similarly releasing these latter acids in the combustion chamber, can also be employed in accordance with the invention to extend the anti-knock effect of lead alkyls in the gasoline.

A large number of other hydrocarbon monocarboxylic acids, including various isoparaffin (branched-chain alkane) monocarboxylic acids, alkyl-substituted aromatic monocarboxylic acid, aryl-substituted paraffin (alkane) monocarboxylic acids, and the like, have been tested, and the results of these tests confirmed their operativeness as additives capable of extending the effect of lead alkyls in the gasoline toward achievement of higher octane numbers. Complete enumeration of all the acids and of all the organic materials which can provide these acids in the combustion chamber of a spark-ignition engine in accordance with the invention would unduly augment the text of this specification. Therefore, examples of operativeness in leaded gasolines of a sufficient number of typical effective hydrocarbon monocarboxylic acids and of representative organic materials which provide them in the combustion chamber will be presented later on in this specification together with the octane rating increment data obtained in various test runs with these lead extender materials in different gasolines in accordance with the known CFR Research and ASTM Motor methods for octane number determination.

As pointed out hereinbefore, the presence of certain substituents and the particular position of these substituents on the hydrocarbon portion of the monocarboxylic acid molecule may affect its ability of enhancing or extending the anti-knock effect of lead in a spark-ignition engine. Thus, α -, γ - and Δ -hydroxy-substituted monocarboxylic acids which are prone to form cyclic lactides or lactones at the temperatures prevailing in the combustion chamber, for example, glycolic acid and lactic acid, are

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ineffective as lead extenders. On the other hand, those of the hydroxy-substituted monocarboxylic acids which do not form cyclic lactides or lactones, e.g., β -hydroxy-isovaleric acid, are effective.

A number of monocarboxylic acids containing an oxy($-\text{O}-$) linkage in the molecule also constitute effective lead extenders in accordance with the invention, whether this oxy linkage is present in a cyclic structure, as in the case of furoic acid; or joining a substituent to the hydrocarbon portion a hydrocarbon monocarboxylic acid thus forming a monocarboxy ether, as in alkoxy-substituted acids, e.g., in methoxyacetic, ethoxyacetic, α -ethoxypropionic, o-methoxybenzoic; or, as in aryloxy-substituted acids, e.g., phenoxybenzoic, naphthoxyacetic; or, as in acyloxy-substituted acids, e.g., acetyl glycolic, acetyl lactic, etc.

In addition to the increase of the octane rating due to the action of these monocarboxylic acids containing oxy linkages, effectively extending the anti-knock effect of the lead alkyl additive in high-octane gasolines, these acids under certain conditions of engine operation provide a secondary advantageous effect in that they facilitate the removal of carburetor and manifold gums. Acyloxy-substituted monocarboxylic acids, e.g., acetyl lactic acid, are particularly preferred in this instance.

Dicarboxylic acids are generally inoperative, an exception being those dicarboxylic acids which decompose below about 225°C . to yield a monocarboxylic acid; for instance, malonic acid decomposes at about 140 – 150°C . and liberates carbon dioxide and acetic acid which is an effective lead extender. By the same token, alkyl malonic acids are suitable as lead extenders.

Monoalkyl esters of dicarboxylic acids, which are thermally stable at about 200°C . and do not form metal chelates, for instance, ethyl acid adipate, behave as free monocarboxylic acids and are therefore effective lead extenders.

The lead extenders of the invention can also be introduced into leaded gasolines in the form of different materials which, at the temperatures existing in the combustion chamber of a spark-ignition engine, decompose and release in that chamber an operative free monocarboxylic acid known not to form metal chelates and to be thermally stable at temperatures below the temperature necessary to fire the gasoline-air mixture.

These monocarboxylic acid "source" materials must likewise be dispersible in gasoline, free of sulfur, chlorine and bromine constituents, and unreactive with lead alkyls at temperatures up to about 40°C ., i.e., prior to being introduced into the engine.

Particularly effective groups of these acid "source" materials are tertiary alcohol esters of monocarboxylic acids, ammonium and amine salts of such acids, their anhydrides and mixed anhydrides.

Tertiary alcohol esters which release free monocarboxylic acids acting as lead extenders include all esters formed by the reaction of tertiary alcohols with monocarboxylic acids, e.g., terpinyl alcohol esters, tertiary butyl esters, pinacol esters, and the like.

Operative ammonium and amine salts of monocarboxylic acids likewise include all such salts which release in the combustion chamber a free monocarboxylic acid effective as a lead extender in accordance with the invention. Among them, there may be mentioned N-methyl anilinium propionate, anilinium benzoate, pyridinium benzoate, ammonium naphthenate, triethylammonium acetate, t-butylammonium actanoate, and the like.

All anhydrides which at the combustion chamber temperatures decompose and yield a free monocarboxylic acid, by splitting out a ketene, or by some other mechanism, can be successfully employed in leaded gasolines as lead extenders in accordance with the invention. Examples of effective anhydrides are naphthenic acid anhydride, mixed acetic-benzoic acid anhydride, mixed formic-acetic anhydride, etc.

In all events, whether employing free monocarboxylic acids as such or organic materials providing these acids in the combustion chamber, the additive in order to enhance effectively the anti-knock action of the lead should be introduced into gasoline in such amounts that the mole ratio of the additive to the lead in the gasoline would lie within the range from about 3:1 to about 60:1, and preferably from about 5:1 to about 30:1.

As mentioned before in this specification, an extension evaluation program has been carried out in the laboratory on different leaded gasolines to test the operativeness of a great number of diverse monocarboxylic acids and organic materials capable of liberating such acids in accordance with the invention. The tests were conducted in single-cylinder CFR knock-test engines in conformity with the accepted procedure for evaluating the anti-knock quality of gasolines, namely, Research method D-908 and Motor method D-357, as described in "ASTM manual of Engine Test Methods for Rating Fuels."

EXAMPLE I

This example describes a test series which employed a leaded gasoline of the following composition: 43% by volume of aromatic hydrocarbons; 16% by volume of

olefins and 41% by volume of paraffins (substantially all branched-chain paraffins). At 3 cc./gal. of TEL this gasoline had a Research octane number of 99.5 and a Motor octane number of 87.6. Ordinarily similar gasolines in this high octane number range respond very poorly, if at all, to further additions of TEL for the purpose of increasing their octane rating. In this test series, the effect of lead extenders in the same gasoline but containing amounts of TEL other than 3 cc. per gallon and with no TEL has also been evaluated. Different monocarboxylic acids have been added to the gasoline in amounts within the operative range of mole ratios of the acid to the lead from about 3:1 to about 60:1. The effect of these additions on the octane rating are tabulated in the following Table I, in which the concentration of the organic acid additive is given in millimols per kilogram (mM./kg.) of gasoline, while the concentration of TEL is given in cc. per gallon of gasoline. For selecting effective concentrations of the acid additive, 3 cc. of TEL per gallon of gasoline is equal to 5.45 milligram-atoms of lead metal per kilogram of gasoline. Symbols $\Delta F-1$ and $\Delta F-2$ designate, respectively, the change in the Research and Motor octane numbers. In practically all of the runs the values of $\Delta F-1$ and $\Delta F-2$ represent averages of four determinations.

TABLE I.—EFFECT OF ADDITION OF MONOCARBOXYLIC ACIDS ON OCTANE RATING

Run No.:	Kind	Monocarboxylic acid added		$\Delta F-1$	$\Delta F-2$
		Conc. in mM./kg.	Conc. of TEL in cc./gal.		
1.....	Acetic.....	167	0	-0.1	
2.....	do.....	33	0	-0.1	
3.....	do.....	17	3	0.5	0.4
4.....	do.....	33	3	1.3	
5.....	do.....	50	3	2.0	
6.....	do.....	67	3	2.2	1.7
7.....	do.....	83	3	2.5	2.2
8.....	do.....	125	3	1.6	
9.....	do.....	167	3	1.1	1.0
10.....	do.....	250	3	0.9	
11.....	do.....	333	3	-0.1	-0.3
12.....	do.....	500	3	-0.6	
13.....	do.....	1,000	3	-1.5	
14.....	do.....	33	6	1.6	
15.....	do.....	83	6	3.2	
16.....	do.....	167	6	4.0	3.9
17.....	do.....	234	6	2.5	
18.....	do.....	333	6	1.9	
19.....	Propionic.....	50	1	0.6	
20.....	do.....	50	3	2.3	
21.....	do.....	135	3	1.9	
22.....	Butyric.....	44	0	0.0	
23.....	do.....	44	3	2.3	1.7
24.....	Benzoic.....	50	1	0.3	
25.....	do.....	41	3	1.7	
26.....	do.....	50	3	2.1	1.7
27.....	do.....	70	3	1.4	
28.....	do.....	93	3	1.2	1.1
29.....	Mixed naphthenic acids ¹	20	3	0.6	0.8
30.....	do.....	48	3	1.8	1.5
31.....	do.....	70	3	2.3	1.8
32.....	do.....	120	3	1.8	1.7
33.....	do.....	240	3		-0.2
34.....	Octanoic.....	42	6	1.8	1.3
35.....	do.....	126	6	3.8	3.7
36.....	do.....	208	6	2.7	3.2
37.....	Isobutyric.....	44	3	0.4	
38.....	Trimethylacetic.....	49	3	1.7	
39.....	β , β -Dimethylacrylic.....	80	3	1.2	
40.....	Cyclohexane carboxylic.....	80	3	2.2	
41.....	2-ethylhexanoic.....	42	3	1.5	
42.....	m-Toluic.....	80	3	1.8	
43.....	t-Butylbenzoic.....	80	3	1.6	
44.....	Crotonic.....	46	3	2.0	
45.....	Phenylacetic.....	43	3	0.9	
46.....	Acrylic.....	80	3	2.6	
47.....	Salicylic.....	24	3	-1.6	
48.....	Oleic.....	80	3	1.4	
49.....	Lauryl acid maleate.....	53	3	-0.3	
50.....	Chloroacetic.....	42	3	-3.3	
51.....	β -Chloropropionic.....	80	3	-0.9	
52.....	Trichloroacetic.....	30	3	-4.2	
53.....	α -Hydroxydecanoic.....	80	3	0.0	
54.....	Pyruvic.....	80	3	-0.6	
55.....	Methoxyacetic.....	44	3	1.4	
56.....	do.....	133	3	2.9	
57.....	o-Toluic.....	40	3	1.6	
58.....	Diethylacetic.....	50	3	2.0	
59.....	Acetyl glycolic.....	57	3	0.7	
60.....	Ethyl acid adipate.....	80	3	2.0	
61.....	Acetyl lactic.....	95	3	1.7	
62.....	Trifluoroacetic.....	44	3	-1.7	
63.....	do.....	132	3	-3.0	
64.....	2-ethylhexyl acid phthalate.....	80	3	-0.7	
65.....	Nitroacetic.....	48	3	-0.1	
66.....	Methacrylic.....	80	3	1.5	
67.....	do.....	110	3	0.7	

¹ Average molecular weight about 250.

The results presented in the above table clearly indicate the improvement of octane rating caused by the addition of free monocarboxylic acids to leaded gasolines in accordance with the invention. As emphasized before, this improvement is achieved only in a leaded gasoline; where the lead is absent, as in runs 1, 2 and 22, no improvement is possible. The octane value increases with the increasing concentration of monocarboxylic acid for the same concentration of lead in the gasoline (e.g., runs 3 to 6), reaches a maximum value (run 7), and then begins to decrease on further increase of the concentration of monocarboxylic acid (runs 8 to 10) until the upper limit of the operative mole ratio of acid to lead in the gasoline (about 60:1) is exceeded, at which time the octane number change becomes a decrement. The same pattern is noted in the data with other acids, for instance, naphthenic, benzoic, propionic, octanoic, etc.

Additionally, it is noted that the increase of octane number is a function of the concentration of lead in the gasoline, and that in the region of maximum improvement, i.e., in the region corresponding to the preferred range of mole ratios of the acid to the lead from about 5:1 to about 30:1, this increase is nearly directly proportional to the concentration of the lead alkyl anti-knock additive in the gasoline. This is illustrated by the attached drawing, in which the concentrations of lead extended (in this particular instance, of acetic acid) are plotted as abscissae and the changes in Research octane number ($\Delta F-1$) are plotted as ordinates. The direct relationship between $\Delta F-1$ and the concentration of lead is clearly apparent from the comparison of the two curves in the drawing: one for gasoline containing 3 cc. of TEL, and the other containing 6 cc. of TEL.

Referring again to the data in Table I, it is observed that, in conformity with the previously given definitions of operative monocarboxylic acids, purely hydrocarbon acids, whether saturated or unsaturated, acyclic aliphatic or cycloaliphatic, aromatic, alkyl aromatic or aryl aliphatic, all act as extenders of the anti-knock property of lead alkyl additives in gasolines.

Substituted monocarboxylic acids containing an oxy(—O—) linkage such as alkoxy-, aryloxy- and acyloxy-substituted monocarboxylic acids, exemplified in Table I by methoxyacetic acid, acetyl glycolic acid and acetyl lactic acid (runs 55, 56, 59, 61) provide a positive octane number increment. Stable monoesters of dicarboxylic acids, which are thermally stable in the combustion chamber during the pre-flame oxidation stage and thus act as free monocarboxylic acids, as represented in this table by ethyl acid adipate (run 60), likewise impart a positive octane number increment.

On the other hand, metal chelate-forming monocarboxylic acids and those monocarboxylic acids which decompose (decarboxylate) in the combustion chamber before firing of the gasoline-air mixture without yielding a free monocarboxylic acid, for instance, salicylic acid (run 47), pyruvic acid (run 54), 2-ethylhexyl acid phthalate (run 64), α -hydroxydecanoic acid (run 53), lauryl acid maleate (run 49), nitroacetic acid (run 65), and so forth, are found to be inoperative.

In agreement with the previously given definitions, monocarboxylic acids which contain chlorine or bromine are found to detract from the octane value instead of improving the same (runs 50, 51, and 52).

The results of test runs made with leaded gasolines containing organic acids which, in accordance with previously given definitions of the invention, are inoperative because of their structure, reactivity, thermal stability, or tendency to decarboxylate, have not been all included in the data of Table I, owing to the limitations of space. Among such inoperative acids, there may be mentioned: formic, oxalic, succinic, adipic, azelaic, glycolic, diglycolic, isophthalic, terephthalic, α -hydroxy-isobutyric, o-chlorobenzoic, bromoacetic, p-aminobenzoic, anthranilic, thioglycolic, cyanoacetic, o-nitrobenzoic, etc.

In some cases, a particular monocarboxylic acid cannot be used as such in leaded gasoline because of its reactivity with lead alkyls before the introduction of the gasoline into the combustion chamber. However, it often happens that an organic material capable of releasing such monocarboxylic acid in the combustion chamber is unreactive with lead alkyls at temperatures up to 40° C. For instance, trifluoroacetic acid (runs 62, 63), or fluoro-benzoic acid, added directly to gasoline are ineffective as lead extenders, but their tertiary alkyl esters are effective.

EXAMPLE II

In another test series, the leaded gasoline, employed in testing the various monocarboxylic acids was of the following composition: 23% by volume of aromatics, 77% by volume of branched-chain paraffins and 6% by volume of n-heptane. The octane number of this gasoline, for a TEL content of 3 cc. per gallon, was 100.7 (Research).

In this case again, addition of the free monocarboxylic acids operative in accordance with the invention resulted in an improvement of the octane rating. To illustrate: 50 mM./kg. of propionic acid added to this gasoline imparted an increment $\Delta F-1$ equal to 2.5 octane numbers. A like addition of benzoic acid provided a $\Delta F-1$ equal to 2.7 octane numbers.

EXAMPLE III

In this test series, an aviation gasoline, composed of 94% by volume of branched-chain paraffins and about 6% by volume of aromatics and containing 3.7 cc./gal. of TEL, had an initial octane number of 92.0 (Research). Addition of 33, 67, 83 and 100 mM./kg. of acetic acid resulted in the following incremental values of $\Delta F-1$: 0.6, 1.9, 1.2 and 1.0. Thus, it is seen that the addition of a free monocarboxylic acid to a leaded gasoline provides an enhancement of the octane rating, whenever the gasoline contains at least about 5% by volume of aromatics or olefins in accordance with the invention.

EXAMPLE IV

In this case, gasoline subjected to testing was composed of 26% aromatics, 30% olefins and 44% by volume of branched-chain paraffins. It had an initial octane Research number of 99.0 for a TEL content of 3 cc./gal. Here again, addition of 33 mM./kg. of acetic acid provided an increment $\Delta F-1$ equal to 1.2 octane numbers (Research); addition of 50 mM./kg. of propionic acid provided a corresponding increment of 0.8 octane numbers; addition of 44 mM./kg. of butyric acid increased the octane rating by 1.2, while benzoic acid, added in an amount of 50 mM./kg., raised the rating by 2 octane units.

Several test series were conducted with synthetic gasolines formed entirely by aromatic or olefinic hydrocarbons.

EXAMPLE V

Here 80 mM./kg. of acetic acid, added to a synthetic wholly olefinic gasoline (essentially 1-hexene) containing the conventional amount of 3 cc./gal. of TEL and characterized by an initial Research octane number of 92.3, imparts an increment $\Delta F-1$ equal to 0.6 to the initial octane rating.

EXAMPLE V-a

In a test series with another wholly olefinic synthetic gasoline (essentially 2-ethyl-1-butene) containing the same amount of TEL (3 cc./gal.) and having an initial Research octane number of 99.0, a like addition of 80 mM./kg. of acetic acid causes an octane rating increment equal to 1.5 octane units.

EXAMPLE VI

In similar tests with synthetic gasolines of wholly aromatic nature (toluene, cumene, and the like), likewise containing 3 cc./gal. of TEL and having an octane number of the order of about 100, addition of acetic

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acid (80 mM./kg.), provides an increase in the octane rating of the order of 2 numbers and higher.

EXAMPLE VI-a

In a test with an entirely cycloparaffinic synthetic gasoline (methylcyclopentane), having a TEL content of 3 cc./gal. and an initial octane number (Research) of 103.9, addition of 80 mM./kg. of acetic acid provides an octane number increment of 1.4.

EXAMPLE VI-b

In the test runs with wholly acyclic isoparaffinic gasoline stocks obtained by HF alkylation of petroleum fractions and having a TEL content of 3 cc./gal., addition of 80 mM./kg. of acetic acid does provide an increment of the octane rating only after the initial Research octane rating approaches the value of 105.0.

EXAMPLE VII

In this example, the gasoline employed for testing the effectiveness of free monocarboxylic acids as lead extenders comprised 36% of aromatics, 23% of olefins and 41% by volume of branched-chain paraffins. Its Research octane rating for a TEL content of 3 cc./gal. was equal to about 99.9. The motor octane rating was 87.8. Addition of 2-ethylhexanoic acid in amounts of 40, 60 and 100 mM./kg. to this gasoline provided an increment of the Research octane number equal to 1.3, 1.7 and 1.5, and a corresponding increment in the Motor octane number equal to 1.0, 1.3 and 1.1, respectively. Addition of benzoic acid to the same gasoline in amounts of 30, 50 and 70 mM./kg. resulted in increments of Research octane number equal to 1.3, 2.0 and 2.4, and corresponding increments of Motor octane number of 1.1, 1.3 and 1.6, respectively.

EXAMPLE VIII

This time the tests were made using a gasoline which contained 2.8 cc./gal. of TEL and had the following com-

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position: 29% aromatics, 22% olefins and 49% by volume of paraffins (mainly branched-chain paraffins, 5 to 10% cycloparaffins). The initial Research octane rating of this gasoline, was 98.0; the Motor rating was 86.2.

Additions of 33, 83 and 167 mM./kg. of acetic acid resulted in corresponding increments $\Delta F-1$ equal to 0.3, 1.2 and 0.2. For 83 mM./kg. of the acid added, the Motor rating was increased by 2.2. Addition of 44 mM./kg. of butyric acid to the same gasoline increased the Research octane rating by 0.9.

In another extensive test series, various esters of tertiary alcohols, capable of supplying a free monocarboxylic acid effective as a lead extender in the combustion chamber in accordance with the invention, have been added to different leaded gasolines and then tested in single-cylinder CFR knock-test engines in accordance with the Research and Motor methods referred to hereinbefore. In addition, a number of non-tertiary esters and other ester-like derivatives of organic acids, which cannot provide an effective free monocarboxylic acid in the combustion chamber, were tested for the sake of contrast.

EXAMPLE IX

The following tabulation of the results obtained in a large number of illustrative test runs clearly shows the operativeness of esters which provide a free monocarboxylic acid as a lead extender in accordance with the invention. These particular esters are esters of tertiary alcohols and monocarboxylic acids which do not form metal chelates, are stable at temperatures incidental to preflame oxidation, contain no sulfur, chlorine or bromine, and are unreactive with lead alkyls at temperatures up to about 40° C. In this first series of tests with esters, the gasoline had the same compositions as the one employed in the tests of Example I, that is, it contained 43% aromatics, 16% olefins and 41% by volume of branched-chain paraffins.

TABLE II.—EFFECT OF ADDITION OF ESTERS ON OCTANE RATING

Run No.	Kind	Ester added		$\Delta F-1$	$\Delta F-2$
		Cone. in mM./kg.	Cone. TEL in cc./gal.		
1.....	t-Butyl acetate.....	40	3	0.5	0.8
2.....	do.....	50	3	0.7	0.8
3.....	do.....	60	3	0.9	0.9
4.....	do.....	82	3	0.7	-----
5.....	do.....	95	3	1.0	-----
6.....	do.....	103	3	1.2	-----
7.....	do.....	172	3	1.1	-----
8.....	do.....	344	3	0.9	-0.2
9.....	Pinacol diacetate.....	25	3	0.4	-----
10.....	(2-methyl pentane diol-2,4)diacetate.....	25	3	0.4	-----
11.....	Methyl acetate.....	81	3	-0.6	-----
12.....	α, α -Dimethylphenyl ethyl acetate.....	61	3	1.1	-----
13.....	t-Butyl trimethyl acetate.....	63	3	1.0	-----
14.....	t-Butyl benzoate.....	56	3	1.4	-----
15.....	do.....	70	3	-----	1.1
16.....	do.....	100	3	0.9	-----
17.....	t-Butyl propionate.....	77	3	0.9	-----
18.....	t-Butyl octanoate.....	50	3	0.9	-----
19.....	t-Amyl acetate.....	58	3	0.7	0.5
20.....	do.....	80	3	0.9	0.8
21.....	do.....	100	3	-----	1.0
22.....	t-Butyl methacrylate.....	42	3	0.9	-----
23.....	do.....	84	3	1.2	-----
24.....	do.....	126	3	1.4	-----
25.....	t-Butyl acetate.....	50	1	0.5	-----
26.....	do.....	172	6	2.9	3.9
27.....	(2-methyl pentane diol-2,4)dipropionate.....	26	3	9.5	-----
28.....	t-Butyl furoate.....	45	3	0.4	-----
29.....	do.....	80	3	0.9	-----
30.....	do.....	95	3	1.3	-----
31.....	Glyceryl diacetate.....	28	3	-0.4	-----
32.....	Phenyl acetate.....	37	3	-0.1	-----
33.....	Vinyl acetate.....	82	3	-0.3	-----
34.....	Benzyl benzoate.....	65	3	-0.2	-----
35.....	Furfuryl acetate.....	43	3	-0.1	-----
36.....	t-Butyl o-chlorobenzoate.....	40	3	-0.4	-----
37.....	do.....	80	3	-1.1	-----
38.....	t-Butyl acetyl glycolate.....	55	3	1.1	-----
39.....	t-Butyl acetyl lactate.....	37	3	1.5	0.7
40.....	do.....	75	3	2.5	1.1
41.....	do.....	117	3	2.0	1.5
42.....	Di-t-butylmalonate.....	80	3	0.5	-----
43.....	t-Butyl o-methoxybenzoate.....	48	3	0.5	-----
44.....	do.....	106	3	1.0	-----
45.....	t-Butyl methyl terephthalate.....	51	3	-0.2	-----
46.....	do.....	106	3	-1.0	-----
47.....	t-Butyl nitroacetate.....	50	3	-3.2	-----
48.....	β -Cyanoethylacetate.....	89	3	0.0	-----

TABLE II—Continued

Run No.	Kind	Ester added		Conc. TEL in cc./gal.	$\Delta F-1$	$\Delta F-2$
		Conc. in mM./kg.	Conc. in mM./kg.			
49.....	t-Butyl o-fluorobenzoate.....	61	3	1.1	-----	
50.....	t-Butyl cyanoacetate.....	35	3	-0.4	-----	
51.....	do.....	106	3	-0.9	-----	
52.....	Phthalide.....	75	3	-0.3	-----	
53.....	β -Isovalerolactone.....	80	3	-0.1	-----	
54.....	Polyester of β -hydroxy isovaleric acid.....	100	3	0.5	-----	
55.....	Di-t-butyl oxalate.....	40	3	-0.7	-----	
56.....	Di-t-butyl adipate.....	40	3	-0.5	-----	
57.....	Di-t-butyl succinate.....	40	3	-0.1	-----	
58.....	Di-t-butyl azelate.....	30	3	-2.0	-----	
59.....	t-Butyl p-nitrobenzoate.....	80	3	1.8	-----	
60.....	t-Butyl m-nitrobenzoate.....	80	3	1.2	-----	
61.....	Terpinylacetate.....	62	3	0.9	-----	
62.....	do.....	83	3	1.2	-----	
63.....	Diethyl glutarate.....	40	3	-0.3	-----	
64.....	Isopropenyl acetate.....	80	3	0.0	-----	
65.....	Propylidene diacetate.....	75	3	0.7	-----	
66.....	t-Butyl m-toluate.....	85	3	1.7	-----	
67.....	t-Butyl methoxyacetate.....	80	3	0.6	-----	
68.....	do.....	120	3	0.7	-----	
69.....	t-Butylacetoxyisobutyrate.....	80	3	1.0	-----	
70.....	t-Butyl cyclohexane carboxylate.....	40	3	0.4	-----	
71.....	do.....	55	3	1.2	-----	
72.....	1,1-dimethylpropinyl acetate.....	60	3	0.7	-----	
73.....	do.....	80	3	1.3	-----	
74.....	do.....	100	3	1.8	-----	
75.....	t-Butyl levulinate.....	40	3	1.1	-----	
76.....	do.....	80	3	1.3	-----	
77.....	do.....	120	3	1.0	-----	
78.....	t-Butyl β -naphthoate.....	80	3	0.8	-----	
79.....	t-Butyl phenoxy acetate.....	80	3	0.7	-----	

The data of Table II show that esters of any tertiary alcohol, whether paraffinic, olefinic or acetylenic, improve the anti-knock quality of leaded gasolines characterized by an initial Research octane number of at least 90, provided the mole ratio of the ester additive to the lead in the gasoline lies in the range from about 3 to about 60, and preferably from about 5 to about 30. Thermally more stable non-tertiary alcohol esters which do not decompose at temperatures incidental to pre-flame oxidation, for instance, methyl acetate (run 11), secondary butyl acetate, phenyl acetate (run 32), vinyl acetate (run 33), and the like, fail to improve the octane rating. Likewise ineffective are esters of tertiary alcohols and monocarboxylic acids which contain chlorine, bromine, and sulfur, for instance, tertiary butyl o-chlorobenzoate (runs 36, 37). Furthermore, in conformity with the definitions of lead extenders operative in accordance with the invention, the data of Table II show inoperativeness of those tertiary esters which, instead of yielding in the combustion chamber prior to firing an operative monocarboxylic acid, decompose to form cyclic compounds, such as lactides or lactones (see runs No. 52 and 53 with phthalide and isovalerolactone). On the other hand, the polymer (polyester) of β -hydroxy isovaleric acid (run No. 54) decomposes, yielding free 3-methyl-2-butenic acid, and is, consequently, effective. Esters of dicarboxylic acids are generally ineffective (e.g., runs 55, 56, 57, 58) unless they decompose and yield a free monocarboxylic acid operative in accordance with the invention (run 42, with di-t-butyl malonate).

EXAMPLE X

In this test series, the gasoline was of the same composition as in Example II above, that is, it contained 23% of the aromatics and 77% by volume of paraffins. The addition of 40, 50 and 60 mM./kg. of t-butyl acetate resulted in the corresponding octane number increases of 1.1, 1.5, 1.8 (Research) and 0.8, 1.7, 2.1 (Motor).

EXAMPLE XI

Another gasoline employed in testing the efficacy of esters of tertiary alcohols in accordance with the invention had the following composition: 36% aromatics, 23% olefins, 41% by volume branched-chain paraffins. With a TEL concentration of 3 cc./gal., it had an initial Research octane rating of 99.9 and a Motor rating of 87.8. The results of several illustrative runs with tertiary alcohol esters are tabulated in Table III below.

In discussing hereinbefore the data of Example I obtained with free monocarboxylic acids, it was noted that the improvement of octane rating due to the addition of the acids was directly proportional to the concentration of lead in the gasoline. The same proportionality is observed with esters of tertiary alcohols, as shown, for instance, by the first nine runs of Table III.

TABLE III

Run No.	Kind	Ester added		Conc. TEL cc./gal.	$\Delta F-1$	$\Delta F-2$
		Conc. in mM./kg.	Conc. in mM./kg.			
40.....	t-Butylacetate.....	40	3	0.5	0.6	
1.....	do.....	80	3	1.2	0.9	
2.....	do.....	100	3	1.6	0.9	
3.....	do.....	80	6	2.4	2.3	
4.....	do.....	120	6	2.9	3.1	
5.....	do.....	160	6	3.2	3.2	
6.....	do.....	78	4.5	1.5	-----	
7.....	do.....	90	4.5	1.6	1.7	
8.....	do.....	120	4.5	1.9	1.8	
45.....	t-Butyloctanoate.....	50	2.5	0.3	1.1	
9.....	do.....	75	2.5	0.4	1.2	
10.....	t-Butylbenzoate.....	40	3	0.3	1.3	
11.....	do.....	50	3	0.8	1.7	
12.....	do.....	65	3	0.3	1.4	
13.....	do.....	50	2.5	0.6	-----	
50.....	t-Butylacetate.....	50	2.5	0.6	-----	

EXAMPLE XII

With 80 mM./kg. of tertiary butyl acetate added to a synthetic, wholly olefinic gasoline (essentially 1-hexene) containing 3 cc./gal. of TEL and having an initial Research octane number of 92.3, the octane rating is increased by 0.4.

EXAMPLE XIII

The same amount (80 mM./kg.) of tertiary butyl acetate added to a leaded synthetic wholly olefinic gasoline (essentially 2-ethyl-1-butene) containing 3 cc./gal. of TEL and having an initial octane rating of 99.0 provides an octane number increment of 0.8.

EXAMPLE XIV

Again the same amount of tertiary butyl acetate as in Examples XII and XIII, added to a leaded gasoline consisting of methylcyclopentane, increases its initial Research octane number of 103.9 by 2.2. This gasoline contained the conventional amount of 3 cc./gal. of TEL.

EXAMPLE XV

This example illustrates the effect of addition of a tertiary alkyl ester of monocarboxylic acid to a leaded (3 cc./gal. TEL) aviation gasoline having a Research

octane number of about 92 and containing 94% branched-chain paraffins and only 6% by volume of aromatics. Addition of 35 mM./kg. of t-butyl acetate secured an octane number increment of 0.4 (Research) and 0.5 (Motor).

Another group of organic materials suitable as lead extenders for leaded gasolines characterized by a Research octane number of at least 90 is formed by gasoline-dispersible organic acid anhydrides which contain no sulfur, chlorine or bromine atoms in their molecular structure, do not react with lead alkyls at temperatures up to about 40° C., and, upon being injected with the leaded gasoline into the combustion chamber of a running spark-ignition engine (in proportions from about 3 to about 60 moles of anhydride per each gram-mole of lead in the gasoline), release therein a free monocarboxylic acid operative as a lead extender in accordance with the invention.

Effective organic acid anhydrides are represented by anhydrides of aliphatic monocarboxylic acids (alkane and alkene monocarboxylic acids), mixed anhydrides of two different aliphatic monocarboxylic acids, and mixed anhydrides of an aliphatic and an aromatic monocarboxylic acid.

EXAMPLE XVI

In this example, different acid anhydrides were tested in a representative gasoline (leaded with 3 cc./gal. of TEL) of mixed composition: 43% aromatics, 16% olefins, 41% by volume branched-chain paraffins. The initial octane ratings of this gasoline were 99.5 (Research) and 87.6 (Motor). The test data obtained are tabulated in Table IV below. All of the anhydrides capable of releasing a free monocarboxylic acid according to the invention improved the octane rating. However, when the anhydride cannot liberate a free acid, as in the case of benzoic anhydride in run 11, no extension of anti-knock effect of lead is obtained.

TABLE IV.—EFFECT OF ADDITION OF ACID ANHYDRIDES ON OCTANE RATING

Run No.	Anhydride added		Conc. TEL cc./gal.	$\Delta F-1$	$\Delta F-2$
	Name	Conc. in mM./kg.			
1	Acetic	40	3	0.8	1.0
2	do	80	3	1.9	1.6
3	do	120	3	2.1	1.4
4	do	140	3	2.1	1.2
5	do	176	3	1.8	1.1
6	do	120	6	3.2	---
7	do	160	3	1.8	1.4
8	do	160	6	4.9	---
9	do	180	3	---	1.1
10	do	200	6	4.5	---
11	do	240	6	2.5	---
12	Propionic	50	3	0.8	---
13	do	80	3	1.7	---
14	Butyric	40	3	0.9	---
15	do	80	3	1.6	---
16	Hexanoic	60	3	1.3	---
17	do	100	3	1.8	---
18	Mixed formicacetic	57	3	2.1	---
19	do	85	3	2.4	---
20	do	142	3	1.7	---
21	Mixed acetic-octanoic	80	3	1.2	---
22	do	108	3	1.6	---
23	Benzoic	50	3	0.0	---
24	Mixed acetic-benzoic	49	3	1.2	---
25	do	110	3	2.3	---

Another class of organic materials operative in accordance with the invention is formed by ammonium and amine salts of monocarboxylic acids, which, added to leaded gasolines having an initial Research octane number of at least about 90, liberate in the combustion chamber a corresponding free monocarboxylic acid devoid of chlorine, bromine or sulfur constituents, forming no metal chelates, and thermally stable at about 200° C. The following several examples illustrate the improvement in octane rating obtained on adding different amine salts to leaded gasolines. Primary, secondary and tertiary aliphatic amine salts, aromatic amine salts, as well as cycloaliphatic amine salts and heterocyclic nitrogen base salts are found to be effective lead extenders in accordance with the invention. There exists

some question in the art as to the true designation of the products of exothermic reaction between aromatic amines and monocarboxylic acids, namely, whether these products actually are amine salts or form complexes with the acids. However, the fact is that these reaction products are homogenous oily liquids, readily soluble in gasoline and distinguishable from simple mixtures of amines and acids by characteristic refractive indexes and electrical conductivities. Therefore, throughout the following description the term "aromatic amine salts" will be employed. All of the aforementioned compounds are salts of monocarboxylic acids and basic nitrogen compounds and include ammonium salts, all of which decompose on being heated to yield free acids. So long as any of these salts is dispersible in a leaded gasoline in concentrations from about 3 to about 60 moles, and preferably from about 5 to about 30 moles, per each gram-atom of lead in the gasoline and does not react with the lead alkyl additive at temperatures up to about 40° C., it will work as an effective lead extender. When such a salt is introduced in leaded gasolines into the combustion chamber of a running spark-ignition engine, the free monocarboxylic acid liberated by the salt acts to extend the effect of the lead as a knock inhibitor in accordance with the principles of this invention, enhancing the octane rating.

EXAMPLE XVII

This example shows the results of a series of test runs using different aliphatic amine salts carried out with the representative leaded gasoline of Example I (43% aromatics, 16% olefins and 41% by volume isoparaffins; initial Research number at 3 cc./gal. of TEL being 99.5).

TABLE V.—EFFECT OF ADDITION OF ALIPHATIC AMINE SALTS ON OCTANE RATING

Run No.	Name	Amine salt added		$\Delta F-1$
		Conc. in mM./kg.	Conc. TEL in cc./gal.	
1	n-Hexyl ammonium octanoate	40	3	1.6
2	Di-n-butylammonium octanoate	40	3	1.4
3	t-Octylammonium acetate	52	3	1.5
4	Triethylammonium acetate	20	3	0.7
5	do	35	3	1.2
6	do	50	3	1.8
7	Triethylammonium octanoate	40	3	1.7
8	t-Butylammonium octanoate	40	3	2.2
9	t-Octylammonium lactate	40	3	-0.1
10	Soyammonium acetate*	33	3	0.3

*A product of reaction between acetic acid and a primary fatty amine derived from soybean oil fatty acids.

It is seen from the above table that the octane rating of gasoline is significantly improved by the introduction of aliphatic amine salts of monocarboxylic acids (alkyl ammonium monocarboxylates). When the amine salt is derived from an acid known to form metal chelates, or when this salt is converted in the combustion chamber prior to firing into a cyclic compound, such as a lactide or a lactone, no enhancement of the octane rating is possible, as demonstrated, for instance, by run 9 of Table V above.

EXAMPLE XVIII

This example illustrates the applicability of ammonium salts of monocarboxylic acids as lead extenders for leaded gasolines in accordance with the invention. In these tests, using the same gasoline as in Example XVII, the introduction, for instance, of 12 mM./kg. of ammonium naphthenate provided an octane number increment of 0.75 (Research), when the lead alkyl (TEL) was present in a concentration of 3 cc./gal. Addition of 25 mM./kg. of the same ammonium naphthenate increased the octane rating by 1.3 (Research).

EXAMPLE XIX

Still in another series of test runs, a large number of aromatic amine salts and heterocyclic nitrogen base salts

of monocarboxylic acids were tested as lead extenders in leaded gasolines, the mole ratio of the amine salt to the lead being from about 3 to about 60, and preferably from about 5 to about 30, as previously specified in describing the invention. The results of several representative test runs are tabulated in Table VI. In these runs a typical gasoline of mixed composition (43% aromatics, 16% olefins and 41% by volume branched-chain paraffins) was employed. The initial octane number of this gasoline without addition of a lead alkyl was 95.6 (Research) and 82.5 (Motor). At a lead content of 3 cc./gal. (as TEL) the octane ratings were 99.5 (Research) and 87.6 (Motor).

TABLE VI.—EFFECT OF ADDITION OF AROMATIC AMINE SALTS ON OCTANE RATING

Run No.	Name	Amine salt added		$\Delta F-1$	$\Delta F-2$
		Conc. in mM./kg.	Conc. TEL in cc./gal.		
1	N-methylanilinium acetate	60	0	0.8	
2	do	33	3		1.4
3	do	60	3	2.6	
4	do	90	3	3.3	
5	do	180	6	5.3	
6	do	180	3	2.6	
7	do	250	3	2.9	
8	do	360	3	2.6	
9	N-methylanilinium formate	61	3	0.0	
10	N-methylanilinium octanoate	40	3	2.3	
11	Anilinium acetate	33	3	0.5	
12	Anilinium benzoate	38	3	1.7	
13	Pyridinium acetate	80	3	2.6	
14	N,N-dimethylanilinium acetate	40	3	1.8	
15	o-Phenylenediammonium octanoate	40	3	3.0	
16	N,N-dimethylanilinium propionate	26	3	0.9	
17	do	104	3	2.2	
18	do	208	3	0.6	
19	N-methylanilinium propionate	52	3	2.9	
20	N-methylanilinium propionate	104	3	3.2	
21	Anilinium propionate	30	3	1.2	
22	do	30	6	1.8	1.4
23	do	60	3	2.5	2.3
24	do	60	6	3.0	2.4
25	do	120	3	2.2	
26	do	120	6	4.8	4.2
27	do	180	3	1.7	
28	do	180	6	4.6	4.6
29	do	360	3	1.6	
30	do	360	6	3.6	3.6

It is known in the art that, in general, aromatic amines inhibit the knock in a spark-ignition engine. The data of Table VI indicate that, upon thermal decomposition of the aromatic amine salts added to leaded gasolines in accordance with the invention, the anti-knock effect owed to the availability of an aromatic amine adds to that owed to the liberation of a free monocarboxylic acid. Again the anti-knock effect is observed to increase with the increasing concentration of lead in the gasoline.

It is seen from the data of the Examples I to XIX that the effectiveness of the lead extender is a function of the concentration of lead in the gasoline, and that at a given level of lead concentration, the response to the addition of lead extender increases with increasing initial Research octane rating of the gasoline and this response

is the better, the higher is the concentration of olefins and/or aromatics in the total composition of gasoline.

It has been pointed out previously in this specification that the beneficial effect of the lead extenders of the present invention is achieved in leaded gasolines having an initial Research octane number of at least about 90, in which lead is present in the form of a lead alkyl, and that TEL has been employed in a majority of the gasolines tested because of its generalized use and availability. However, any other lead alkyl similarly endowed with the property of reducing the knock tendency of gasoline can be used instead of TEL, and in such instances the addition of the anti-knock synergists or lead extenders of

this invention likewise brings about an improvement in the octane rating, as may be seen from the data of the following example.

EXAMPLE XX

In the test series illustrated by this example the composition of gasoline was the same as in Example I (43% aromatics, 16% olefins and 41% by volume paraffins). Different lead alkyls in amounts equivalent to 3 cc./gal. of TEL were employed in this test series as anti-knock additives. Various representative lead extender materials were tested in the resulting leaded gasolines in accordance with the standard CFR Research test method. The results are shown in Table VII.

TABLE VII.—EFFECT OF LEAD EXTENDERS ON OCTANE RATING WITH DIFFERENT LEAD ALKYLs

Run No.	Lead alkyl used	Extender added		$\Delta F-1$
		Kind	mM./kg.	
1	Diisopropyl diethyl lead	Acetic acid	40	1.8
2	do	do	80	3.4
3	do	do	100	3.7
4	do	do	140	3.1
5	do	Acetic-octanoic anhydride	40	2.1
6	do	do	80	3.3
7	do	do	100	2.9
8	do	t-Butyl acetate	60	0.9
9	do	do	100	1.1
10	Tetraisopropyl lead	Acetic acid	40	1.2
11	do	do	80	2.6
12	do	do	140	2.4
13	do	do	160	2.9
14	do	do	40	1.9
15	do	do	80	1.4
16	do	do	100	0.5
17	do	t-Butyl acetate	40	0.1
18	do	do	80	1.9
19	do	do	100	0.1
20	Tetrapropyl lead	Acetic acid	80	2.0
21	do	do	100	1.7
22	do	do	120	1.4

As mentioned hereinbefore, the operativeness of the lead extenders of the present invention has also been checked and confirmed by extensive chassis dynamometer determinations of road octane ratings in conformity with the accepted Modified Uniontown Test Procedure.

In these determinations automobiles of recent manufacture (1956-1957) and of different makes have been employed. The octane requirement of these automobiles at standard timing ranged from about 91 to about 103 octane numbers. Compression ratios varied from 8.5 to 1 as high as 12 to 1. Five road octane ratings were obtained on each base fuel and on the corresponding combination of base fuel and lead extender. The improvement in road rating was calculated as the difference between the averages of these five ratings.

Allowances being made for the variations due to the experimental errors, to the construction differences of the automobile engines and to the differences in air-fuel ratios, the following three representative road rating tests are sufficiently illustrative of the invention.

In the first representative test, using three automobiles, the road octane number of a commercial leaded (3 cc./gal. of TEL) gasoline with an initial Research octane number of 98.0 (86.2, Motor), containing 44% aromatics, 30% olefins and 26% by volume of branched-chain paraffins, to which there was added 50 mM./kg. of propionic acid, was found to be improved by 1.3 road octane numbers (average for all three cars). In another similar test, using five automobiles, the road octane number of a gasoline containing 29% aromatics, 29% olefins and 42% by volume of branched-chain paraffins, leaded with 3 cc./gal. of TEL and characterized by an initial Research octane number of 101.0 (87.7, Motor), to which there was added 50 mM./kg. of t-butyl acetate, was found to be increased by 1.04 road octane numbers (average for all five cars). In another like test, again using five automobiles, the road octane number of a gasoline containing 41% aromatics, 11% olefins and 48% by volume of branched-chain paraffins, similarly leaded with 3 cc./gal. of TEL and characterized by an initial Research octane number of 103.9 (91.9, Motor), to which was added 60 mM./kg. of N-methylaniline propionate, was found to be improved by 1.33 road octane numbers (average for all five cars).

The organic materials suitable for use as lead extenders in high-octane leaded gasolines in accordance with the present invention may be employed either individually or in combination. For instance, an operative aromatic amine salt of a monocarboxylic acid may be combined with an operative ester of a tertiary alcohol and a monocarboxylic acid.

Small proportions of conventional additives to gasolines, such as rust inhibitors, detergents, anti-knock agents other than lead alkyls (for instance, pentacarbonyl derivatives of iron and cyclopentadienyl derivatives of manganese or iron), halogen scavengers, such as ethylene bromide and ethylene chloride, dyes, etc., may be present in leaded gasolines containing the anti-knock synergists or lead extenders of the present invention, provided these additives are compatible with the lead extenders and do not destroy or substantially diminish the beneficial effects thereof.

In concluding, it is emphasized that the test data of the foregoing description are merely illustrative of the invention, and that all variations and modifications may be made therein without detracting from the spirit or the scope of the invention which, consequently, is restricted solely by the purview of the appended claims.

What is claimed is:

1. A knock-resistant leaded gasoline composition for use in spark ignition engines, said composition comprising (1) gasoline containing paraffinic hydrocarbon content of not more than 95% by volume and a minimum Research octane number of about 90; (2) a lead alkyl antiknock additive in an amount from about 0.5 to about

6.0 cc. per gallon of said gasoline; and (3) a small amount, sufficient to extend the antiknock effect of lead in said gasoline, of a gasoline-dispersible, non-corrosive tertiary alcohol ester of a monocarboxylic acid containing only carbon, hydrogen and oxygen in its molecular structure, said ester being inert with respect to lead alkyls at temperatures up to about 40° C., being present in said leaded gasoline in a concentration from about 3 to about 60 moles per gram-atom of lead in the gasoline.

2. A knock-resistant leaded gasoline composition for use in spark ignition engines, said composition comprising (1) gasoline containing a paraffinic hydrocarbon content of not more than 95% by volume and a minimum Research octane number of about 90; (2) a lead alkyl antiknock additive in an amount from about 0.5 to about 6.0 cc. per gallon of said gasoline; and (3) a small amount, sufficient to extend the antiknock effect of lead in said gasoline, of a gasoline-dispersible, non-corrosive tertiary alcohol ester of a monocarboxylic acid containing only carbon, hydrogen and oxygen in its molecular structure, said ester being inert with respect to lead alkyls at temperatures up to about 40° C., being present in said leaded gasoline in a concentration from about 5 to about 30 moles per gram-atom of lead in the gasoline.

3. A knock-resistant leaded gasoline composition for use in spark ignition engines, said composition comprising (1) gasoline containing paraffinic hydrocarbon content of not more than 95% by volume and a minimum Research octane number of about 90; (2) a lead alkyl antiknock additive in an amount from about 0.5 to about 6.0 cc. per gallon of said gasoline; and (3) a small amount, sufficient to extend the antiknock effect of lead in said gasoline, of a gasoline-dispersible, non-corrosive tertiary alkyl ester of a monocarboxylic acid containing only carbon, hydrogen and oxygen in its molecular structure, said ester being inert with respect to lead alkyls at temperatures up to about 40° C., being present in said leaded gasoline in a concentration from about 3 to about 60 moles per gram-atom of lead in the gasoline.

4. A knock-resistant leaded gasoline composition for use in spark ignition engines, said composition comprising (1) gasoline containing paraffinic hydrocarbon content of not more than 95% by volume and a minimum Research octane number of about 90; (2) a lead alkyl antiknock additive in an amount from about 0.5 to about 6.0 cc. per gallon of said gasoline; and (3) a small amount, sufficient to extend the antiknock effect of lead in said gasoline, of a gasoline-dispersible, non-corrosive tertiary butyl ester of a monocarboxylic acid containing only carbon, hydrogen and oxygen in its molecular structure, said ester being inert with respect to lead alkyls at temperatures up to about 40° C., being present in said leaded gasoline in a concentration from about 3 to about 60 moles per gram-atom of lead in the gasoline.

5. A knock-resistant leaded gasoline composition for use in spark ignition engines, said composition comprising (1) gasoline containing paraffinic hydrocarbon content of not more than 95% by volume and a minimum Research octane number of about 90; (2) a lead alkyl anti-knock additive in an amount from about 0.5 to about 6.0 cc. per gallon of said gasoline; and (3) a small amount, sufficient to extend the antiknock effect of lead in said gasoline, of a gasoline-dispersible, non-corrosive tertiary alkyl ester of a hydrocarbon monocarboxylic acid containing only carbon, hydrogen and oxygen in its molecular structure, said ester being inert with respect to lead alkyls at temperatures up to about 40° C., being present in said leaded gasoline in a concentration from about 3 to about 60 moles per gram-atom of lead in the gasoline.

6. A knock-resistant leaded gasoline composition for use in spark ignition engines, said composition comprising (1) gasoline containing paraffinic hydrocarbon content of not more than 95% by volume and a minimum Research octane number of about 90; (2) a lead alkyl antiknock additive in an amount from about 0.5 to about

6.0 cc. per gallon of said gasoline; and (3) a small amount, sufficient to extend the antiknock effect of lead in said gasoline, of a gasoline-dispersible, non-corrosive tertiary alkyl ester of an aromatic monocarboxylic acid containing only carbon, hydrogen and oxygen in its molecular structure, said ester being inert with respect to lead alkyls at temperatures up to about 40° C., being present in said leaded gasoline in a concentration from about 3 to about 60 moles per gram-atom of lead in the gasoline.

7. A knock-resistant leaded gasoline composition for use in spark ignition engines said composition comprising (1) gasoline containing paraffinic hydrocarbon content of not more than 95% by volume and a minimum Research octane number of about 90; (2) a lead alkyl antiknock additive in an amount from about 0.5 to about 6.0 cc. per gallon of said gasoline; and (3) a small amount, sufficient to extend the antiknock effect of lead in said gasoline, of a gasoline-dispersible, non-corrosive tertiary alkyl ester of an aliphatic monocarboxylic acid containing only carbon, hydrogen and oxygen in its molecular structure, said ester being inert with respect to lead alkyls at temperatures up to about 40° C., being present in said leaded gasoline in a concentration from about 3 to about 60 moles per gram-atom of lead in the gasoline.

8. A hydrocarbon fuel in the gasoline boiling range containing a tetraalkyllead antiknock agent, at least 5 volume percent of high octane components selected from the group consisting of olefinic hydrocarbons, aromatic hydrocarbons, and a mixture thereof, and a gasoline-soluble saturated hydrocarbyl monocarboxylic acid in an amount sufficient to further improve the octane rating of said hydrocarbon fuel.

9. A hydrocarbon fuel in the gasoline boiling range containing a tetraalkyllead antiknock agent, at least 5 volume percent of high octane components selected from the group consisting of olefinic hydrocarbons, aromatic hydrocarbons, and mixtures thereof and pinacol diacetate in an amount sufficient to further improve the octane rating of said hydrocarbon fuel.

10. A hydrocarbon fuel in the gasoline boiling range containing a tetraalkyllead antiknock agent, at least 5 volume percent of high octane components selected from the group consisting of olefinic hydrocarbons, aromatic hydrocarbons, and mixtures thereof, and a lower molecular weight alkyl monoester of hydrocarbyl dicarboxylic acid in an amount sufficient to further improve the octane rating of said hydrocarbon fuel.

11. A hydrocarbon fuel in the gasoline boiling range containing a tetraalkyllead antiknock agent, substantial quantities of high octane components selected from the group consisting of olefinic hydrocarbons, aromatic hydrocarbons and mixtures thereof and a tertiary alkyl ester of a hydrocarbyl monocarboxylic acid in a concentration of about 0.1 to about 2.0 volume percent.

12. A hydrocarbon fuel in the gasoline boiling range containing a tetraalkyllead antiknock agent, at least 5 volume percent of high octane components selected from the group consisting of olefinic hydrocarbons, aromatic hydrocarbons and mixtures thereof and a compound selected from the group consisting of acyloxy-substituted hydrocarbyl monocarboxylic acids and tertiary alkyl esters thereof in an amount sufficient to further improve the octane rating of said hydrocarbon fuel.

13. A high octane leaded hydrocarbon fuel in the gasoline boiling range consisting essentially of paraffinic hydrocarbons, having a minimum Research Octane Number of about 105, and containing a minor amount of a hydrocarbyl monocarboxylic acid sufficient to further improve the octane rating of said fuel.

14. A hydrocarbon fuel in the gasoline boiling range containing a tetraalkyl lead antiknock agent, at least 5 volume percent of high octane components selected from the group consisting of olefinic hydrocarbons, aromatic hydrocarbons, and mixtures thereof, and a high base strength amine salt of a hydrocarbyl monocarboxylic acid in an amount sufficient to further improve the octane rating of said hydrocarbon fuel.

15. A hydrocarbon fuel according to claim 8 in which the hydrocarbyl monocarboxylic acid is acetic acid.

16. A hydrocarbon fuel in accordance with claim 10 in which the alkyl monoester of hydrocarbyl dicarboxylic acid is ethyl acid adipate.

17. A hydrocarbon fuel in accordance with claim 11 in which the tertiary alkyl ester of a hydrocarbyl monocarboxylic acid is tertiary butyl acetate.

18. A hydrocarbon fuel in accordance with claim 11 in which the tertiary alkyl ester of a hydrocarbyl monocarboxylic acid is tertiary butyl benzoate.

19. A hydrocarbon fuel in accordance with claim 11 in which the tertiary alkyl ester of a hydrocarbyl monocarboxylic acid is tertiary butyl propionate.

20. A hydrocarbon fuel in accordance with claim 11 in which the tertiary alkyl ester of a hydrocarbyl monocarboxylic acid is tertiary amyl acetate.

21. A hydrocarbon fuel in accordance with claim 11 in which the tertiary alkyl ester of a hydrocarbyl monocarboxylic acid is tertiary butyl methacrylate.

22. A hydrocarbon fuel in accordance with claim 13 in which the hydrocarbyl monocarboxylic acid is acetic acid.

23. A hydrocarbon fuel in accordance with claim 14 in which the amine salt of hydrocarbyl monocarboxylic acid is tertiary octyl ammonium acetate.

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U.S. Cl. X.R.

44—69, 70, 71; 252—386