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MOTOR FUEL CONTAINING AN OCTANE APPRECIATOR

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This invention relates to a hydrocarbon fuel composition of high octane rating. More specifically, it involves the discovery that the octane rating of leaded gasoline fuels of prescribed composition is substantially improved by the addition thereto of acyloxy lactones.

The recent increases in compression ratios of automobile engines have placed a severe strain on petroleum refiners to produce fuels having the octane ratings demanded by these engines. Premium fuels at the present time have research octane ratings between 97 and 101 and it has been predicted that premium fuels will have to have octane ratings between 105 and 110 five years from now in order to satisfy the octane requirements of the high compression automotive engines predicted for that date. In order to produce premium fuels of octane ratings of 95 and above, it has been necessary for refiners to rely heavily on catalytic refining operations such as fluid catalytic cracking, catalytic reforming, alkylation and catalytic isomerization.

Catalytic cracking and catalytic reforming, which are the most widely used refining operations in the production of high octane fuels, produce substantial quantities of aromatics; catalytic cracking also produces a substantial amount of olefins. It is well known that olefins and aromatics, although possessing high octane ratings, have a poorer response to organo-lead compounds such as tetraethyl lead than saturated aliphatic gasoline components. Accordingly, as the aromatic and olefinic content of the gasolines have increased to meet the octane levels required by modern automotive high compression engines, the lead response of the resulting fuels has diminished. Stated another way, the octane increment obtainable by the addition of an organo-lead compound decreases as the aromatic and olefin contents of the base fuel increase. The subject invention involves the discovery that the octane rating of leaded motor fuels containing a substantial concentration of high octane components, that is, aromatic, olefins and mixtures thereof, is markedly improved by the addition of a small amount of acyloxy lactones of prescribed composition.

In a commonly-assigned copending application, Serial No. 689,466, filed October 11, 1957, by G. W. Eckert, it is disclosed that hydrocarbyl monocarboxylic acids substantially raise the octane rating of a motor fuel containing an organo-lead anti-knock agent and a substantial concentration of high octane components which may be aromatic hydrocarbons, olefinic hydrocarbons or mixtures thereof. In a series of cases filed subsequent to the afore-identified copending application it is disclosed that this octane appreciating action in the leaded fuels of prescribed composition is also possessed by a number of acid derivatives such as tertiary alkyl esters and acid anhydrides which are converted to hydrocarbyl monocarboxylic acids at the conditions prevailing in the engine during combustion. In a commonly-assigned copending application, Serial No. 772,184, filed November 6, 1958, by R. Y. Heisler and G. W. Eckert, it is disclosed that lactones of prescribed composition are effective octane appreciators for leaded fuels. The subject invention involves the discovery that certain acyloxy-substituted lactones are also effective octane appreciators for leaded motor fuel compositions having the prescribed aromatic and/or olefin content.

The high octane hydrocarbon motor fuel of this invention comprises high octane components including a substantial concentration of aromatic hydrocarbons, olefinic hydrocarbons and mixtures thereof, an organo-lead anti-knock agent and an acyloxy lactone wherein the acyloxy radical is substituted on the carbon atom joined to the oxygen bridge of the lactone. The acyloxy lactones are present in the leaded fuel in concentrations between 0.1 and 5.0 volume percent.

The action of acyloxy lactones in appreciating the octane rating of gasoline is characterized by several unusual features. In the first instance, these compounds are ineffective in raising the octane rating of gasoline unless an organo-lead anti-knock agent, normally tetraethyl lead, TEL, is a component of the gasoline mixture. The second unusual characteristic of their action in appreciating the octane rating of gasolines is the fact that an equivalent concentration of acyloxy lactone causes a greater octane improvement above the 100 octane level than below the 100 octane level. The third unusual feature of the action of acyloxy lactones is that they appear to have substantially little effect on the octane rating of a gasoline consisting essentially of saturated aliphatic hydrocarbons even though an organo-lead anti-knock agent is present.

Since organo-lead anti-knock agents exert their greatest octane appreciation in predominantly saturated paraffinic base hydrocarbon gasolines and have the least effect on the octane rating of aromatic and olefin-rich gasolines, the present invention neatly complements tetraethyl lead as an octane improver. Acyloxy-substituted lactones have their minimum effect where tetraethyl lead has its maximum effect and exert their maximum effect on octane values where tetraethyl lead has its minimum effect.

The novel fuel compositions of this invention have a minimum concentration of aromatic and/or olefin components of at least 5 volume percent. The aromatic and/or olefin components of the motor fuel of the invention can constitute as high as 100 volume percent thereof but usually comprise between 20 and 80 volume percent. A 5 percent concentration of aromatics and/or olefins appears to be necessary for acyloxy lactones to exert a significant octane improvement.

The aromatic components of the motor fuel of the invention are generally supplied by catalytic reforming or catalytic cracking operations. Catalytic reformate is particularly high in aromatics. The olefin components of the motor fuel of the invention are derived either from thermal cracking, catalytic cracking or polymerization.

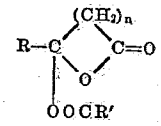
The organo-lead reagent necessary for the action of acyloxy lactones as octane improvers is usually a tetraalkyl lead compound. Tetraethyl lead is universally used as an anti-knock agent but other tetraalkyl lead compounds such as tetramethyl lead, tetrabutyl lead, tetraamyl lead, tetrapropyl lead, etc., possess anti-knock properties and are used in the fuel compositions of the invention in conjunction with acyloxy lactones.

The tetraethyl lead mixtures commercially available for automotive use contain an ethylene chloride-ethylene bromide mixture as a scavenger for removing lead from the combustion chamber in the form of volatile lead halides. Tetraethyl lead fluid, the commercial product, comprises tetraethyl lead, ethylene chloride and ethylene bromide, the latter two reagents being present in 1.0 theory and 0.5 theory, respectively, theory denoting the stoichiometric amount required for reaction with the lead content of the tetraethyl lead.

The organo-lead reagent is present in the fuel compositions of the invention in concentrations between 0.5 ml. per gallon up to the statutory limit of organo-lead reagent concentration which, at the present time, is 4 ml. per gallon in the case of automotive fuel and 4.6 ml. per gallon

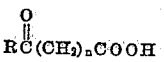
in the case of aviation fuel. The usual concentration of tetraethyl lead is between 1 and 3 ml. per gallon in automotive gasoline and 2 to 4.6 ml. per gallon in aviation gasoline. An octane appreciating action is obtained with acyloxy lactones at TEL concentrations of 6 ml. per gallon and higher.

The acyloxy lactones which are effective in increasing the octane rating of aromatic and olefin containing leaded gasolines have the acyloxy radical attached to the carbon atom joined to the oxygen bridge of the lactone. These acyloxy lactones have the following general formula:

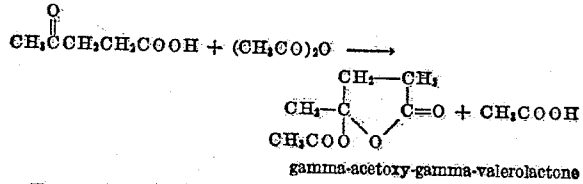


in which R is a hydrogen atom or a C_1 to C_{10} hydrocarbyl radical, R′ is a hydrocarbyl radical containing 1 to 11 carbon atoms and n is an integer having a value of 2 or 3. R is advantageously a hydrogen atom or a C_1 to C_5 alkyl group and R′ is advantageously a C_1 to C_6 aliphatic hydrocarbyl radical.

Acyloxy lactones which are effective as octane appreciators are formed by reaction of an aldehyde or ketone of the general formula:



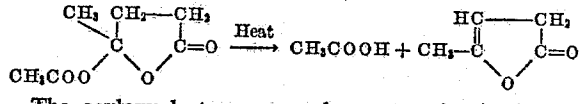
wherein R is a hydrogen or a C_1 to C_{10} hydrocarbyl radical and n has a value of 2 or 3 with an anhydride of a monocarboxylic acid containing 2 to 12 carbon atoms. The following equation illustrates the reaction between levulinic acid and acetic anhydride to form an acyloxy lactone effective as an octane appreciator.



gamma-acetoxy-gamma-valerolactone

Examples of effective lactone esters containing an acyloxy radical substituted on the carbon atom attached to the oxygen bridge of the lactone are the following: gamma-acetoxy-gamma-butyrolactone, gamma-propionoxy-gamma-valerolactone, delta-acetoxy-delta-valerolactone, gamma-butyroxy-gamma-caprolactone, delta-benzoxy-delta-caprylolactone.

The effectiveness of lactones containing an acyloxy radical substituted on the carbon atom joined to the oxygen bridge is believed to result from the fact that they readily decompose under the conditions existing during oxidation of the gasoline in the internal combustion engine to form unsaturated derivatives of heterocyclic oxygen compounds and hydrocarbyl monocarboxylic acids which latter are the effective octane appreciating agents. This decomposition is illustrated in the following equation showing the decomposition of gamma-acetoxy-gamma-valerolactone.



The acyloxy lactones must be present in the leaded aromatic and/or olefin-containing compositions of the invention in a minimum concentration of 0.1 volume percent before a significant octane appreciation is realized. When the concentration of the acyloxy lactone is below 0.1 volume percent, there is no noticeable octane improvement in leaded gasolines of prescribed composition. The preferred concentration of acyloxy lactone falls between 0.2 and 2.0 volume percent with maximum octane appreciation generally being obtained at concentrations between 0.5 and 1.5 volume percent. Although concentrations of acyloxy lactone as high as 5 volume percent may be employed, economic considerations preclude the use of such high concentrations. In addition, it appears that there is a significant decrease in octane appreciating action after the acyloxy lactone concentration exceeds about 2.0 volume percent.

In Table I there is shown the effectiveness of the acyloxy lactones of prescribed composition in raising the octane rating of a leaded fuel composition containing the prescribed aromatic and/or olefin content. The base fuel employed in Table I had a research octane number (RON) of 105, a motor octane number (MON) of 98.5 and comprised approximately 10 volume percent n-butane, 40 percent isobutylene-isobutane alkylate, 10 percent pentenes from fluid catalytically cracked naphtha and 40 percent heavy platformate; the base fuel contained 3 cc. of TEL per gallon. Fluorescent indicator analysis (FIA) of the 105 octane base fuel indicated an aromatic content of approximately 35 percent and an olefin content of approximately 6 percent; its initial boiling point (IBP) was 90° F. and its end point was 367° F.

TABLE I

Octane increase in 105 RON fuel by acyloxy lactones

	Increase in RON
Base fuel+0.25 v. percent gamma-acetoxy-gamma-valerolactone	0.2
Base fuel+0.5 v. percent gamma-acetoxy-gamma-valerolactone	0.7
Base fuel+0.75 v. percent gamma-acetoxy-gamma-valerolactone	1.3

The data in the above table show the effectiveness of acyloxy lactones in appreciating the octane rating of leaded fuels containing at least 5% aromatics and/or olefins.

In Table II there is shown the octane appreciating action of acyloxy lactones in a commercial premium motor fuel having an RON of 100.3. The premium motor fuel employed in Table II contains 3 cc. of TEL per gallon and had an IBP of 89° F. and an end point of 372° F. FIA indicated that it comprised 53% saturated hydrocarbons, 38% aromatics and 9% olefinic hydrocarbons.

TABLE II

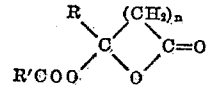
Octane increase in premium fuel by acyloxy lactones

	Increase in RON
Base fuel+0.5 v. percent gamma-acetoxy-gamma-valerolactone	1.2
Base fuel+0.75 v. percent gamma-acetoxy-gamma-valerolactone	1.4

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A hydrocarbon fuel in the gasoline boiling range containing an organo-lead anti-knock agent, high octane components selected from the group consisting of olefinic hydrocarbons, aromatic hydrocarbons and mixtures thereof in a concentration of at least 5.0 volume percent of said fuel, and an acyloxy lactone having the general formula



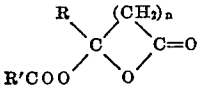
in which R is selected from the group consisting of hydrogen and hydrocarbyl radicals containing 1 to 10 carbon atoms, R′ is a hydrocarbyl radical containing 1 to 11 carbon atoms and n is an integer selected from the group consisting of 2 and 3, said acyloxy lactone being present in a concentration between 0.1 and 5.0 volume percent

which concentration is sufficient to effect substantial octane appreciation of said leaded fuel.

2. The hydrocarbon fuel according to claim 1 in which said organo-lead anti-knock agent is present in a concentration between 0.5 and 4.6 cc. per gallon.

3. The hydrocarbon fuel according to claim 1 in which said acyloxy lactone is present in a concentration between 0.2 and 2.0 volume percent.

4. A hydrocarbon fuel in the gasoline boiling range containing an alkyl lead anti-knock agent in a concentration of at least 0.5 cc. per gallon, high octane components selected from the group consisting of olefinic hydrocarbons aromatic hydrocarbons and mixtures thereof in a concentration of at least 5.0 volume percent of said fuel and an acyloxy lactone of the general formula:



wherein R is selected from the group consisting of hydrogen and a hydrocarbyl radical containing 1–10 carbon atoms, R′ is a hydrocarbyl radical containing 1–11 carbon atoms and n is an integer selected from the group consisting of 2 and 3, said acyloxy lactone being present in a concentration between 0.1 and 5.0 volume percent, said concentration being sufficient to effect substantial improvement in the octane rating of said fuel.

5. The hydrocarbon fuel according to claim 4 in which said acyloxy lactone is present in a concentration between 0.2 and 2.0 volume percent.

6. The hydrocarbon fuel according to claim 4 in which said high octane components constitute 20–80 volume percent of said fuel.

7. The hydrocarbon fuel according to claim 4 containing 1.0 to 4.6 cc. tetraethyl lead per gallon.

8. The hydrocarbon fuel according to claim 4 in which said acyloxy lactone is gamma-acetoxy-gamma- valerolactone.

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