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MOTOR FUEL CONTAINING OCTANE IMPROVER

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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 is substantially improved by the addition of a lactone.

The recent increases in compression ratios of automobile engines have placed a severe strain on petroleum refiners to produce fuels having the octane rating demanded by these engines. Premium fuels at the present time have research octane ratings between 97 and 100 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, aromatics, olefins and mixtures thereof, is markedly improved by the addition of a small amount of a lactone.

In copending application Serial No. 689,466 filed October 11, 1957, it is disclosed that 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. The subject invention involves the discovery that lactones of monohydroxy monocarboxylic acids exert a similar anti-knock action in gasoline of the prescribed composition.

The high octane hydrocarbon motor fuel of this invention comprises a substantial concentration of aromatic hydrocarbons, olefinic hydrocarbons, or mixtures thereof, an organo-lead anti-knock agent and a lactone of a monohydroxy monocarboxylic acid in a concentration of at least 0.1 volume percent of the fuel.

The action of lactones in raising the octane rating

of gasoline is characterized by several unusual features. In the first instance, the lactones appear to be ineffective in raising the octane rating of gasolines unless an organo-lead anti-knock agent, normally tetraethyl lead, is a component of the gasoline mixture.

The second unusual characteristic of the action of lactones in appreciating the octane rating of gasolines is the fact that an equivalent concentration of lactone appears to cause a greater octane improvement above the 100 octane level than below the 100 octane level.

The third unusual feature of the action of lactones is that they appear to have substantially no 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. 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.

Another surprising feature of the action of lactones as octane appreciators is that hydroxy monocarboxylic acids are ineffective in improving the octane rating of leaded fuels containing the prescribed aromatic and/or olefin content.

The novel fuel compositions of this invention have a minimum concentration of aromatic and/or olefin components of at least 10 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. Approximately a 10 percent concentration of aromatic and/or olefins is necessary for 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.

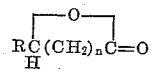
The organo-lead reagent necessary for the action of lactones as octane improvers is a tetraalkyl lead compound of the class known to possess anti-knock action. Tetraethyl lead is universally used as an anti-knock agent but other tetraalkyl lead compounds such as tetramethyl lead, tetrabutyl lead, tetraamyl lead, tetrapropyl lead, etc. possess anti-knock properties and may be used in the fuel compositions of the invention in conjunction with 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. As is used hereafter in the examples illustrating the invention, "tetraethyl lead fluid" denotes the commercial product which 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 3 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.

The lactones which are effective in increasing the octane rating of an aromatic and/or olefin-containing leaded gasoline have the general formula:



wherein R is hydrogen or a hydrocarbyl radical containing 1–27 carbon atoms and *n* has a value of 1–4 and usually 2 to 3. The R radical can be an aliphatic hydrocarbon radical, an aromatic hydrocarbon radical or a cycloaliphatic hydrocarbon radical or it can be a mixed radical such as an aralkyl or an alkaryl radical. Lactones effective as octane appreciators in the fuel compositions of the invention are the following: gamma-butyrolactone, gamma-valerolactone, beta-propiolactone, delta-valerolactone, delta-phenyl-gamma-valerolactone-1,4, delta-caprolactone, omega-tolyl-delta-caprolactone, omega-cyclohexyl - gamma - valerolactone, delta - caprylolactone and delta-laurolactone. The preferred lactones are those formed from hydroxy monocarboxylic acids containing 3–10 carbon atoms.

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 lactones is below 0.1 volume percent, no octane improvement is obtained in leaded gasoline containing 10 or more volume percent aromatics and/or olefins. The preferred concentration of lactones in the fuel compositions of the invention fall between 0.2 and 2.0 volume percent with maximum octane appreciation generally being obtained at concentration levels between 0.5 and 1.5 volume percent. There is a fall-off in octane appreciation as the concentration exceeds about 1.5 volume percent. Concentrations of lactones as high as 5 volume percent can be employed but economic considerations coupled with the lower octane improvement realized at the higher concentrations dictate against the use of such concentrations in commercial fuel compositions.

In Table I data are presented to show the effectiveness of lactones in raising the octane rating of the leaded fuel compositions containing the prescribed aromatic and/or olefin content. The data in Table I also shows the ineffectiveness of hydroxy monocarboxylic acids. The base fuel to which the lactones were added in Table I was a catalytically reformed naphtha containing 3 cc. of TEL fluid per gallon and having an IBP of 130° F. and an end point of 394° F. The base fuel had a leaded Research Octane Number (RON) of 96.6 and an aromatic content of 48 volume percent as measured by Fluorescent Indicator Analysis (FIA) method.

Table I

	Research Octane Values—Volume Percent of Additive in 96.6 RON Fuel		
	0.25	0.50	1.0
β-propiolactone	97.2	97.3	97.4
γ-butyrolactone	97.2	97.1	97.4
γ-valerolactone	97.2	97.4	
ricinoleic acid		96.6	
salicylic acid		96.6	

The data in the above table indicate clearly that lactones are effective octane appreciators for leaded fuels of the prescribed composition whereas hydroxy monocarboxylic acids such as ricinoleic acid and salicylic acid are ineffective as octane appreciators. Lower molecular weight hydroxy monocarboxylic acids, such as hydroxy butyric acid, were too insoluble in gasoline to give a fuel containing the minimum 0.1 volume percent concentration required for octane appreciation.

In Table II there is shown the action of beta-propiolactone in improving the octane rating of 105 RON gasoline. The base fuel contained 3 cc. of TEL fluid per gallon and comprised approximately 10 percent n-butane, 40 percent isobutane-isobutylene alkylate, 10 percent pentenes from fluid catalytically cracked naphtha and 40 percent heavy platformate. The 105 RON base fuel had an aromatic content of approximately 35 percent and an olefin content of approximately 6 percent and had an IBP of 90° F. and an end point of 367° F.

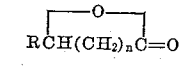
Table II

	Research octane values
Base fuel	105.3
Base fuel+0.5 v. percent beta-propiolactone	105.7
Base fuel+0.75 v. percent beta-propiolactone	106.0
Base fuel+1.0 v. percent beta-propiolactone	106.3

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:

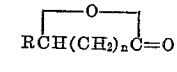
1. A hydrocarbon fuel in the gasoline boiling range containing an organo-lead anti-knock agent, high octane components selected from the group consisting of olefinic hydrocarbons, aromatic hydrocarbons and mixtures thereof in a concentration of at least 10 volume percent, and a lactone having the general formula



wherein R is selected from the group consisting of hydrogen and a hydrocarbyl radical containing 1–27 carbon atoms and *n* has a value of 1–4, said lactone being present in a concentration of 0.1 to 5.0 volume percent, said amount being sufficient to effect substantial improvement of the octane rating of said organo-lead-containing hydrocarbon fuel.

2. A 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. A hydrocarbon fuel in the gasoline boiling range containing a tetraalkyl 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 10 volume percent of said fuel and a lactone having the general formula:



wherein R is selected from the group consisting of hydrogen and a hydrocarbyl radical containing 1–27 carbon atoms and *n* has a value of 1–4 in a concentration of 0.1 to 5.0 volume percent.

4. A hydrocarbon fuel according to claim 3 in which the concentration of said lactone is between 0.2 and 2.0 volume percent.

5. A hydrocarbon fuel according to claim 3 in which said high octane components constitute 20–80 volume percent of said fuel.

6. A hydrocarbon fuel according to claim 3 in which said lactone is beta-propiolactone.

7. A hydrocarbon fuel according to claim 3 in which said lactone is gamma-butyrolactone.

8. A hydrocarbon fuel according to claim 3 in which said lactone is gamma-valerolactone.

(References on following page)

References Cited in the file of this patent

UNITED STATES PATENTS

1,692,784	Orelup et al.	Nov. 20, 1928
2,210,942	Lipkin	Aug. 13, 1940
2,228,662	Holm	Jan. 14, 1941

FOREIGN PATENTS

640,311	France	Mar. 26, 1928
837,965	France	Nov. 28, 1938
277,326	Great Britain	Jan. 7, 1929

OTHER REFERENCES

"Aviation Gasoline Manufacture," by Van Winkle, first ed., McGraw-Hill Book Co., 1944, pages 200–205 and 212–223.

"Organic Chemistry," by Karrer, third ed., Elsevier Pub. Co., 1947, page 254.

"Improved Motor Fuels Through Selective Blending," Wagner et al., paper presented before American Petroleum Institute, Nov. 7, 1941, pages 1–19.