

1

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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 fuel is substantially improved by the addition of aldehyde dialkanoates.

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 a Research Octane Rating between 97 and 100 and it has been predicted that premium fuels will require 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 97 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 aromatic and/or olefinic components is markedly improved by the addition of a small amount of an aldehyde dialkanoate.

In our commonly assigned copending application Ser. No. 689,466 filed Oct. 11, 1957, it is disclosed that hydrocarbyl monocarboxylic acids substantially raise the octane rating of a motor fuel containing an organo-lead anti-knock agent in a substantial concentration of high octane components which may be aromatic hydrocarbons, olefinic hydrocarbons, or mixtures thereof. Another commonly assigned copending application, Ser. No. 699,944 filed Dec. 2, 1957, discloses that t-alkyl esters of monocarboxylic acids have a similar octane appreciating action on leaded fuels of prescribed composition. This invention involves the discovery that another class of esters are effective octane appreciators in leaded fuels of prescribed composition.

The high octane hydrocarbon motor fuels of this invention comprise high octane components including a substantial concentration of aromatic hydrocarbons, olefinic hydrocarbons, or mixtures thereof, an organo-lead anti-knock agent, and aldehyde dialkanoates in a concentration of at least 0.1 volume percent of the fuel.

The action of aldehyde dialkanoates in raising the octane rating of gasoline is characterized by several unusual features. In the first instance, the aldehyde dialkanoates appear to be ineffective in raising the octane rating of

2

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 aldehyde dialkanoates in appreciating the octane rating of gasolines is the fact that an equivalent concentration of additive 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 aldehyde dialkanoates 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. Aldehyde dialkanoates 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 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. The minimum 10 percent concentration is necessary for aldehyde dialkanoates 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 operation. 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 aldehyde alkanates 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 aldehyde dialkanoates.

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" is a commercial product comprising tetraethyl lead, ethylene chloride and ethylene bromide, the later two reagents being present in amounts equivalent to 1.0 theory and 0.5 theory, respectively, where theory is 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 aldehyde dialkanoates which are effective in increasing the octane rating of an aromatic and/or olefin-containing leaded gasoline have the general formula: $RCH=OOCR'$ wherein R is selected from the group consisting of a hydrocarbyl radical containing 1-12 carbon atoms and a furyl radical and R' is an aliphatic hydrocarbyl radical containing 1-12 and preferably 1-8

carbon atoms; the two R's can be the same or different aliphatic hydrocarbyl radicals. The aldehyde dialkanoates effective as octane appreciators are prepared by reacting an aldehyde such as acetaldehyde or benzaldehyde with acetic anhydride in the presence of an acid catalyst such as concentrated sulfuric acid.

Aldehyde dialkanoates effective as octane appreciators in the fuel compositions of the invention are the following: Benzaldiacetate, benzaldipropionate, benzaldibutyrate, benzaldi-2-ethylhexanoate, benzaldilaurate, acetaldehyde diacetate, acetaldehyde dipropionate, acetaldehyde dihexanoate, isobutyraldehyde diacetate, isobutyraldehyde diisobutyrate, isobutyraldehyde dipropionate, 2-ethylhexaldehyde diacetate, 2-ethylhexaldehyde diisobutyrate, 2-ethylhexaldehyde dipropionate, furfuraldiacetate and furfuraldipropionate.

The preferred aldehyde dialkanoates used in the fuel compositions of the invention are derived from aldehydes containing 1-8 carbon atoms and from aliphatic monocarboxylic acids containing 1-8 carbon atoms. Preferred aldehyde dialkanoates are acetaldehyde diacetate, benzaldiacetate, benzaldipropionate, acetaldehyde dipropionate, propionaldehyde diacetate and furfuraldiacetate.

The aldehyde dialkanoates 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 aldehyde dialkanoates 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 aldehyde dialkanoates in the fuel compositions of the invention fall between 0.2 and 2.0 volume percent with maximum octane appreciation generally being obtained at concentrations between about 0.5 and 1.5 volume percent. Although concentrations of aldehyde dialkanoates as high as 5 volume percent may be employed with accompanying octane appreciation, economic considerations preclude the use of such high concentrations. In addition, it appears there is a fall-off in octane appreciation after the concentration of the aldehyde dialkanoate exceeds about 1.5 volume percent.

In the following table there is shown the effectiveness of aldehyde dialkanoates as octane appreciators in a leaded base fuel comprising approximately 10 percent n-butane, 40 percent isobutane-isobutylene alkylate, 10 percent pentenes from fluid catalytically cracked naphtha and 40 percent heavy platformate. With 3 cc. of tetraethyl lead (TEL) per gallon, this base fuel had a Research Octane No. (RON) of 105. Fluorescent Indicator Analysis (FIA) indicated that this base fuel had an aromatic content of approximately 35 percent and an olefinic content of approximately 6 percent, its IBP was 90° F. and its end point was 367° F.

Table I

	Research octane No.
Base fuel -----	105.0
Base fuel +0.25 v. percent benzaldiacetate -----	105.6
Base fuel +0.5 v. percent benzaldiacetate -----	106.3
Base fuel +1.0 v. percent benzaldiacetate -----	107.4
Base fuel +0.25 v. percent acetaldehyde diacetate -----	105.6
Base fuel +0.5 v. percent acetaldehyde diacetate --	105.7
Base fuel +1.0 v. percent acetaldehyde diacetate --	107.5
Base fuel +0.5 v. percent furfuraldiacetate -----	106.4
Base fuel +1.0 v. percent furfuraldiacetate -----	107.3

The data in Table I indicate the effectiveness of acetaldehyde diacetate in improving the octane rating of a leaded fuel containing the prescribed aromatic and/or olefin content.

In Table II there is shown the effectiveness of aldehyde diacetates in improving the octane rating of a commercial premium gasoline comprising approximately 39

percent saturates, 30 percent olefins and 31 percent aromatics. This commercial premium base fuel contained 3 cc. of TEL per gallon and had an RON of 99.0.

Table II

	Research octane No.
Base fuel -----	99.0
Base fuel +0.5 v. percent benzaldiacetate -----	99.2
Base fuel +1.0 v. percent benzaldiacetate -----	99.5
Base fuel +1.0 v. percent acetaldehyde diacetate -----	100.2
Base fuel +0.5 v. percent furfuraldiacetate -----	99.3
Base fuel +1.0 v. percent furfural diacetate -----	99.4
The specificity of aldehyde diacetates in appreciating the octane rating of leaded fuels containing the prescribed aromatic and/or olefin content was demonstrated by the fact that the polyol esters shown in Table III were ineffective in improving the octane rating of a leaded fuel containing the prescribed aromatic and/or olefin content.	

Table III

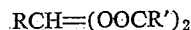
Polyol esters ineffective as octane appreciators in concentrations up to 1.0 vol. percent:

25	Sucrose octaacetate
	Pentaerythritol tetraacetate
	Ethylene glycol diformate
	Ethylene glycol diacetate
	Ethylene glycol dilaurate
30	Ethylene glycol dimyristate
	Ethylene glycol dipalmitate
	2,2,4-trimethyl 1,3-pentane diacetate.

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, at least 10 volume percent of high octane components selected from the group consisting of olefinic hydrocarbons, aromatic hydrocarbons and mixtures thereof and an aldehyde dialkanoate in a concentration of 0.1 to 5.0 volume percent, said concentration being sufficient to effect substantial improvement of the octane rating of said hydrocarbon fuel said aldehyde dialkanoate having the general formula:



- wherein R is selected from the group consisting of a hydrocarbyl radical containing 1-12 carbon atoms and the furyl radical and R' is an aliphatic hydrocarbyl radical containing 1-12 and preferably 1-8 carbon atoms.

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 an aldehyde dialkanoate having the general formula: $RCH=(OOCR')_2$ wherein R is selected from the group consisting of a hydrocarbyl radical containing 1-12 carbon atoms and the furyl radical and R' is an aliphatic hydrocarbyl radical containing 1-12 and preferably 1-8 carbon atoms, said aldehyde dialkanoate being present in a concentration of 0.1 to 5.0 volume percent.

4. A hydrocarbon fuel according to claim 3 in which said aldehyde dialkanoate is present in a concentration 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.

5

6

6. A hydrocarbon fuel according to claim 3 containing 1.0 to 4.6 cc. of tetraethyl lead per gallon.

7. A hydrocarbon fuel according to claim 3 in which said aldehyde dialkanoate is benzaldiacetate.

8. A hydrocarbon fuel according to claim 3 in which said aldehyde dialkanoate is acetaldehyde diacetate.

9. A hydrocarbon fuel according to claim 3 in which said aldehyde dialkanoate is furfural diacetate.

10. A hydrocarbon fuel in the gasoline boiling range containing a tetraalkyl lead antiknock agent, substantial quantities of high octane components selected from the group consisting of olefinic hydrocarbons, aromatic hydrocarbons and mixtures thereof and ethylidene diacetate in an amount sufficient to improve the octane rating of said hydrocarbon fuel.

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