

1

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MOTOR FUEL CONTAINING OCTANE APPRECIATOR

Harry Chafetz, Poughkeepsie, and George W. Eckert and Alfred Arkell, Wappingers Falls, N.Y., assignors to Texaco Inc., New York, N.Y., a corporation of Delaware

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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 particular group of esters of hydroxy substituted heterocyclic oxygen compounds.

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, aromatic, olefins and mixtures thereof, is markedly improved by the addition of a small amount of certain esters of hydroxydioxane and hydroxytetrahydropyran of prescribed composition.

In 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 aforeidentified 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. The subject invention involves the discovery that certain esters of heterocyclic oxygen compounds also have an octane appreciating action in leaded motor fuel compositions of this type.

The high octane hydrocarbon motor fuel of this invention comprises high octane components including a sub-

2

stantial concentration of aromatic hydrocarbons, olefinic hydrocarbons and mixtures thereof, an organo-lead anti-knock agent and a hydrocarbyl ester of a hydroxydioxane or a hydroxytetrahydropyran in which the acyloxy radical is on a nuclear carbon atom adjacent to a nuclear carbon atom substituted with at least one hydrogen atom. The nuclear carbon containing the acyloxy radical is preferably joined to a nuclear oxygen atom. The dioxane and tetrahydropyran esters of prescribed type are present in the leaded fuel in a concentration between 0.1 and 5.0 volume percent.

The action of these hydroxydioxane and hydroxytetrahydropyran esters in appreciating the octane rating of gasoline is characterized by several unusual features. In the first instance, these esters 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 the action of these esters in appreciating the octane rating of gasolines is the fact that an equivalent concentration of dioxane or tetrahydropyran esters causes a greater octane improvement above the 100 octane level than below the 100 octane level. The third unusual feature of the action of these hydroxydioxane and hydroxytetrahydropyran esters 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. Hydroxydioxane and hydroxytetrahydropyran esters 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 hydroxydioxane and hydroxytetrahydropyran esters 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 reformat 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 hydroxydioxane and hydroxytetrahydropyran esters 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 may be used in the fuel compositions of the invention in conjunction with hydroxydioxane and hydroxytetrahydropyran esters.

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 stoichio-

3

metric 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.

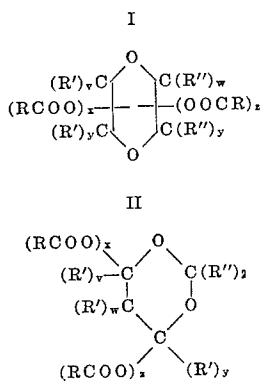
The esters of hydroxydioxanes and hydroxytetrahydropyrans which are effective in increasing the octane rating of aromatic and olefin-containing leaded gasoline are derived from a hydrocarbyl monocarboxylic acid containing 1 to 30 carbon atoms and a hydroxy-substituted dioxane or a hydroxy-substituted tetrahydropyran in which the hydroxy radical is on a nuclear carbon atom adjacent to a nuclear carbon containing at least one hydrogen substituent. The ester-containing nuclear carbon atom preferably is attached to a nuclear oxygen atom.

The hydrocarbyl monocarboxylic acids employed in the formation of effective ester octane appreciators can be aliphatic, cycloaliphatic or aryl monocarboxylic acids of the general formula: RCOOH wherein R denotes a hydrogen atom or a hydrocarbyl radical containing 1 to 29 carbon atoms. Preferred monocarboxylic acids employed in the formation of effective hydroxydioxane and hydroxytetrahydropyran esters contain 1 to 8 carbon atoms and are either an aliphatic or aryl monocarboxylic acid. Examples of preferred acids used in the formation of the esters are acetic acid, propionic acid, n-butyric acid, valeric acid, n-hexanoic acid, 2-ethylhexanoic acid, benzoic acid and toluic acid.

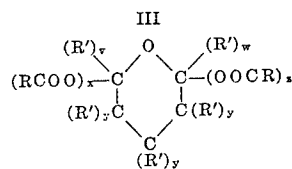
The esters of the hydroxydioxanes and hydroxytetrahydropyrans must have at least 1 hydrogen atom on a carbon atom adjacent to the nuclear carbon atom containing the ester group. The ester group preferably is also attached to a nuclear carbon atom joined to a nuclear oxygen atom.

Hydroxy substituted 1,3-dioxanes and hydroxy substituted 1,4-dioxanes both form monocarboxylic acid esters effective as octane appreciators. Hydroxy-1,3-dioxanes useful in the formation of esters effective as octane appreciators are most readily obtained by condensation of acetaldehyde and propionaldehyde in the presence of alkaline catalysts. 2,4-dimethyl-6-hydroxy-1,3-dioxane is obtained by trimerization of acetaldehyde and 2,4-diethyl-5-methyl-6-hydroxy-1,3-dioxane is obtained by trimerization of propionaldehyde. Both of these compounds form effective esters since they both contain a hydrogen atom on a nuclear carbon adjacent to the carbon atom containing the hydroxyl substituent and also have the ester group attached to a nuclear carbon atom joined to a nuclear oxygen atom.

The effective hydroxydioxane and hydroxytetrahydropyran esters can be represented by one of the three general formulae:



4



wherein R is a hydrogen atom or a hydrocarbyl radical containing 1-29 carbon atoms, R' and R'' are a hydrogen atom or an aliphatic hydrocarbyl radical containing 1-8 carbon atoms, v, w, x, y, and z having the values 0, 1, or 2, the total of $v+w+x+y+z$ being 8 in Formula I, 6 in Formula II and 10 in Formula III and at least one R' on a carbon atom adjacent to the nuclear carbon containing the acyloxy radical, $\text{RCOO}-$, being a hydrogen atom.

Example of the effective esters are the following: 2-acetoxy-1,4-dioxane, 2-benzoxy-1,4-dioxane, 2-propionyloxy-1,4-dioxane, 4-acetoxy-1,3-dioxane, 4-lauroxy-1,3-dioxane, 2,4-dimethyl-6-acetoxy-1,3-dioxane, 2,4-dimethyl-6-benzoxy-1,3-dioxane, 2,4-dimethyl-6-propionyloxy-1,3-dioxane, 2,4-diethyl-5-methyl-6-acetoxy-1,3-dioxane, 2,4-diethyl-5-methyl-6-isooctanoxy-1,3-dioxane, 2,3-diacetoxy-1,4-dioxane, and 2-acetoxy-3-methyl-1,4-dioxane. Examples of effective esters of hydroxytetrahydropyran are the following: 2-acetoxytetrahydropyran, 2,3-diacetoxytetrahydropyran, 2-acetoxy-3-methyltetrahydropyran, 2-propionyloxy-4-ethyltetrahydropyran.

It has been theorized that the esters of hydroxydioxane and hydroxytetrahydropyran in which the acyloxy radical is attached to a nuclear carbon atom which is adjacent to a nuclear carbon atom containing at least one hydrogen atom and is preferably joined to a nuclear oxygen atom are effective octane appreciators because under conditions existing during oxidation of the fuel in the internal combustion engine they decompose to give hydrocarbyl monocarboxylic acids and unsaturated derivatives of dioxane and tetrahydropyran. Esters such as 2,4-diisopropyl-5,5-dimethyl-6-acetoxy-1,3-dioxane, an ester of hydroxydioxane compound formed by trimerization of isobutyraldehyde, which does not contain a hydrogen atom on the nuclear carbon atom adjacent to the nuclear carbon containing the acyloxy radical, is ineffective as an octane appreciator. This latter compound cannot readily decompose on heating to yield a monocarboxylic acid and an unsaturated heterocyclic oxygen derivative.

The hydroxydioxane and hydroxytetrahydropyran esters 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 esters is below 0.1 volume percent, there is no noticeable octane improvement in leaded gasolines of prescribed composition. The preferred concentration of hydroxydioxane and hydroxytetrahydropyran ester 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 the ester of hydroxydioxanes and hydroxytetrahydropyrans as high as 5 volume percent may be employed, economic considerations preclude the use of such high concentrations. In addition, it appears there is a significant decrease in octane appreciating action after the ester concentration exceeds about 2.0 volume percent.

In Table I there is shown the effectiveness of the hydroxydioxane and hydroxytetrahydropyran esters 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

Increase in Research Octane Number by Esters of Hydroxy Di-Oxanes and Hydroxytetrahydropyrans in 105 RON Fuel

	Increase in RON
Base Fuel+0.5 v. percent 2,4-dimethyl-6-acetoxy-1,3-dioxane	1.3
Base Fuel+0.75 v. percent 2,4-dimethyl-6-acetoxy-1,3-dioxane	2.3
Base Fuel+1.0 v. percent 2,4-dimethyl-6-acetoxy-1,3-dioxane	2.5
Base Fuel+0.75 v. percent 2,4-diethyl-5-methyl-6-acetoxy-1,3-dioxane	1.3
Base Fuel+0.5 v. percent 2-acetoxytetrahydropyran	2.2
Base Fuel+0.75 v. percent 2-acetoxytetrahydropyran	2.9
Base Fuel+1.0 v. percent 2-acetoxytetrahydropyran	2.7
Base Fuel+0.7 v. percent 2,3-diacetoxy-1,4-dioxane	2.1
Base Fuel+0.5 v. percent 2,4-diisopropyl-5,5-dimethyl-6-acetoxy-1,3-dioxane	0.0

The data in the above table show the effectiveness of esters of hydroxydioxanes and esters of hydroxytetrahydropyrans in appreciating the octane rating of leaded fuels containing the prescribed aromatic and/or olefinic content. All of the effective esters contain a hydrogen atom on the nuclear carbon adjacent to the nuclear carbon atom containing the ester group and also have the ester group attached to a nuclear carbon joined to a nuclear oxygen atom. The ineffective ester, namely 2,4-diisopropyl-5,5-dimethyl-6-acetoxy-1,3-dioxane does not meet this requirement.

In Table II there is shown the octane appreciating action of esters of hydroxydioxanes and of hydroxytetrahydropyrans of prescribed composition in a commercial premium motor fuel having an RON of 100.9. The premium motor fuel employed in Table II contained 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 approximately 50 percent saturated hydrocarbons, 30 percent aromatics and 20 percent olefinic hydrocarbons.

TABLE II

Units Improvement in Octane Rating of Premium Fuel by Esters of Hydroxydioxanes and of Hydroxypyrans

	Increase in RON
Base Fuel+0.75 v. percent 2,4-dimethyl-6-acetoxy-1,3-dioxane	1.3
Base Fuel+0.5 v. percent 2,3-diacetoxy-1,4-dioxane	1.8
Base Fuel+0.7 v. percent 2,3-diacetoxy-1,4-dioxane	1.1
Base Fuel+0.5 v. percent 2,4-diisopropyl-5,5-dimethyl-6-acetoxy-1,3-dioxane	0.0

The data in Table II confirmed the specificity of the octane appreciating action of hydroxydioxane esters and of hydroxytetrahydropyran esters to compounds of prescribed composition. Comparison of the data in Tables I and II also show that equivalent concentrations of the hydroxydioxane esters are more effective in higher octane base fuels.

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 5 volume percent high octane components selected from the group consisting of olefinic hydrocarbons, aromatic hydrocarbons and mixtures thereof and a hydrocarbyl ester of a heterocyclic oxygen compound selected from the group consisting of esters of hydroxydioxane and hydroxytetrahydropyran wherein the acyloxy radical is attached to a nuclear carbon atom joined to a nuclear oxygen atom and a nuclear carbon atom having at least one hydrogen substituent, said ester being present in the 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 hydrocarbyl ester is present in a concentration between 0.2 and 2.0 volume percent.
3. 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.
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 ester of a hydrocarbyl monocarboxylic acid containing 1-8 carbon atoms and a heterocyclic oxygen compound selected from the group consisting of hydroxydioxane and hydroxytetrahydropyran in a concentration between 0.1 and 5.0 volume percent of said fuel, said ester containing the acyloxy radical attached to a nuclear carbon atom which is joined to a nuclear oxygen atom and to a nuclear carbon atom having at least one hydrogen substituent.
5. The hydrocarbon fuel according to claim 4 in which the concentration of said ester is 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. of tetraethyl lead per gallon.
8. The hydrocarbon fuel according to claim 4 in which said ester is 2,4-dimethyl-6-acetoxy-1,3-dioxane.
9. The hydrocarbon fuel according to claim 4 in which said ester is 2,4-diethyl-5-methyl-6-acetoxy-1,3-dioxane.
10. The hydrocarbon fuel according to claim 4 in which said ester is 2-acetoxy-tetrahydropyran.
11. The hydrocarbon fuel according to claim 4 in which said ester is 2,3-diacetoxy-1,4-dioxane.

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