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MOTOR FUEL CONTAINING AN OCTANE APPRECIATOR

George W. Eckert, Wappingers Falls, Stanley R. Newman, Fishkill, Kenneth L. Dille, Wappingers Falls, and Norman Alpert, Poughkeepsie, N.Y., assignors to Texaco Inc., 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 of prescribed composition is substantially improved by the presence therein of glycol esters containing an acyloxy radical attached to a tertiary carbon atom.

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 olefinic 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 glycol esters of prescribed composition.

In 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 and a substantial concentration of high octane components which may be aromatic hydrocarbons, olefinic hydrocarbons or mixtures thereof. In another commonly-assigned copending application Ser. No. 699,944, filed Dec. 2, 1957, it is disclosed that t-alkyl esters of hydrocarbyl monocarboxylic acids have a similar octane appreciating action in leaded motor fuels of the same composition. The subject invention involves the discovery that glycol esters containing at least one acyloxy radical attached to a tertiary carbon atom of the glycol residue also have an octane appreciating action in motor fuel compositions of the prescribed type.

The high octane hydrocarbon motor fuel of this invention comprises high octane components including a substantial concentration of aromatic hydrocarbons, olefinic hydrocarbons or mixtures thereof, an organo-lead anti-knock agent and a glycol ester containing at least one acyloxy radical attached to a tertiary carbon atom of the glycol. The glycol ester of prescribed composition is present in a minimum concentration of 0.1 volume percent in the motor fuel of the invention. The glycol esters can be monoesters or diesters as long as one acyloxy radical is attached to a tertiary carbon atom of the glycol portion of the molecule.

The action of glycol esters having at least one acyloxy radical attached to a tertiary carbon atom in appreciating the octane rating of gasoline is characterized by several unusual features. In the first instance, the glycol esters of prescribed composition appear to be 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 glycol esters in appreciating the octane rating of gasolines is the fact that an equivalent concentration of glycol ester 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 glycol esters of prescribed composition is that they appear to have substantially little effect on the octane rating of a gasoline consising 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. Glycol esters having an acyloxy radical attached to a tertiary carbon atom 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. A 10 percent concentration of aromatics and/or olefins appears to be necessary for glycol 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 reforamte 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.

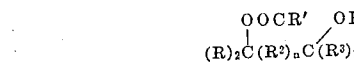
The organo-lead reagent necessary for the action of glycol esters as octane improves is usually a tetraalkyl lead compound. Tetraethyl lead is universally used as an anti-knock agent but other tetraalkyl lead compounds such as tetramethyl lead, tetrabutyl lead, tetraamyl lead, tetrapropyl lead, etc.,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

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 com-

positions 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 glycol esters which are effective in increasing the octane rating of aromatic and olefin-containing leaded gasoline have the general formula:



wherein R is aliphatic hydrocarbyl radical containing 1–8 and preferably 1–4 carbon atoms, R' is a hydrocarbyl radical containing 1–12 carbon atoms and preferably 1–8 cabon atoms, R^2 is a divalent aliphatic hydrocarbyl radical containing 1–6 carbon atoms, R^3 is hydrogen or an aliphatic hydrocarbyl radical containing 1–8 and preferably 1–4 carbon atoms, R^4 is hydrogen or —OCR' wherein R' is defined as previously set forth and n is 0 or 1.

The glycol esters having the above general formula are formed by esterification of a glycol having at least one tertiary hydroxy group with acid anhydrides, acid chlorides, ketene or a hydrocarbyl monocarboxylic acid which is usually an aliphatic acid containing 1–8 carbon atoms or an aryl acid containing 7–8 carbon atoms. Preferred agents for esterification of glycols containing at least one tertiary hydroxy group are acetic acid, propionic acid, 2-ethylhexanoic acid, 2-ethylbutyric acid, benzoic and toluic acid, their anhydrides and chlorides, or ketene.

Glycol diesters of prescribed formula are the preferred octane appreciators although glycol monoesters having an acyloxy radical attached to a tertiary carbon atom are also effective. The diesters are preferred because of their greater gasoline solubility and because of the fact that they contain 2 acid moieties which are believed to be the active octane appreciating components of the glycol ester molecule.

Examples of effective glycol esters having an acyloxy radical attached to a tertiary carbon atom of the glycol molecule are pinacol diacetate, pinacol monoacetate, pinacol dipropionate, pinacol dibenzoate pinacol di-2-ethylhexanoate, pinacol monopropionate, pinacol monobenzoate, pinacol di-2-ethylbutyrate, 2-methyl-2,4-pentanediol diaceate, 2-methyl-2-acetoxy-4-hydroxy pentane hereafter called 2-methyl-2,4-pentanediol monoacetate, 2-methyl-2,4-pentanediol dipropionate, 2-methyl-2,4-pentanediol dibenzoate, 2-methyl-2,4-pentanediol di-2-ethylhexanoate, 2-methyl-2,4-pentanediol monopropionate, 2-methyl-2,4-pentanediol monobenzoate, 3,6-dimethyl-3,6-diacetoxy octyne-4, 3,6-dimethyl-3,6-dipropionoxy octyne-4, 3-ethyl-3,4-hexanediol diacetate, 3-ethyl-3,4-hexanediol dipropionate.

The glycol ester having at least one acyloxy radical attached to a tertiary carbon atom must be present in a minimum concentration of 0.1 volume percent before a signnificant octane appreciation is realized. Below the minimum prescribed concentration of 0.1 volume percent no measurable octane appreciation is obtained in a leaded gasoline containing the prescribed aromatic and/or olefin content. Thep referred concentration of glycol esters falls between about 0.3 and 2.0 volume percent with maximum octane appreciation usually being obtained at a concentration level between 0.5 and 1.5 volume percent. Octane appreciation is obtained with glycol ester concentrations as high as about 4.0 volume percent but economic considerations preculde the use of such concentrations in commercial fuel compositions. Moreover, there appears to be a significant decrease in octane appreciation as the glycol ester concentration exceeds about 1.5 volume percent of the gasoline composition.

In Table I there is shown the effectiveness of glycol 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.—UNITS IMPROVEMENT IN OCTANE RATING BY GLYCOL ESTERS IN 105 OCTANE FUEL

	Increase	
	RON	MON
Base Fuel+0.5 v. percent 2-methyl-2, 4-pentanediol diacetate	2.0	1.2
Base Fuel+0.7 v. percent 2-methyl-2,4-pentanediol monoacetate	1.3	0.9
Base Fuel+0.5 v. percent pinacol diacetate	1.8	----------
Base Fuel+0.5 v. percent pinacol monoacetate	1.4	----------
Base Fuel+1.0 v. percent pinacol monoacetate	2.3	----------

The data in the above table prove the octane appreciating action of glycol esters having an acyloxy radical attached to a tertiary carbon atom in a leaded fuel containing the prescribed aromatic and/or olefin content.

In Table II there is shown the octane appreciating action of glycol esters of prescribed compositions in a commercial premium motor fuel having an RON of 100.4. 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% saturated hydrocarbons, 30% aromatics and 20% olefinic hydrocarbons.

TABLE II.—UNITS IMPROVEMENT IN OCTANE RATING BY GLYCOL ESTERS IN PREMIUM FUEL

	Increase	
	RON	MON
Base Fuel+0.5 v. percent 2-methyl-2,4-pentanediol diacetate	0.8	0.8
Base Fuel+0.7 v. percent 2-methyl-2,4-pentanediol monoacetate	0.4	0.7
Base Fuel+0.5 v. percent pinacol diacetate	1.3	----------

The data in Table II show the effectiveness of glycol esters of prescribed composition in appreciating the octane rating of premium motor fuel. A comparison of the data in Table I with the data in Table II brings out the interesting fact that greater octane appreciation is realized by equivalent concentrations of glycol esters at the 105 octane level than at the 100 octane level. This phenomenon is characteristic of glycol esters as well as of the hydrocarbyl monocarboxylic acids and t-alkyl esters which are the subject matter of the afore-identified Ser. Nos. 689,466 and 699,944, respectively.

In Table III there is shown the action of unsaturated glycol esters having at least one acyloxy radical attached to a tertiary carbon atom in an aviation base fuel containing 4.6 cc. of TEL per gallon. This base fuel, which had an RON of 107.8, was indicated by FIA to have a composition of approximately 61% saturates, 35% aromatics and 4% olefinic hydrocarbons.

TABLE III.—UNITS IMPROVEMENT IN RON BY GLYCOL ESTERS IN A LEADED AVIATION FUEL

	Increase in RON
Base Fuel+0.5 v. percent 3,6-dimethyl-3,6-diacetoxy octyne-4	0.6
Base Fuel+1.0 v. percent 3,6-dimethyl-3,6-diacetoxy octyne-4	2.0

In Table IV there is shown the effect of varying concentrations of a glycol ester of prescribed composition, namely, 2-methyl-2,4-pentanediol diacetate on the octane rating of 2 different high octane fuels. The 105 RON fuel described in Table I is identified as Base Fuel A and the commercial premium gasoline described in Table II is identified as Base Fuel B.

TABLE IV.—UNITS IMPROVEMENT IN OCTANE RATING WITH VARYING CONCENTRATIONS OF 2-METHYL-2,4-PENTANEDIOL DIACETATE

	Increase			
	Base Fuel A		Base Fuel B	
	RON	MON	RON	MON
0.3	1.2	0.5	0.5	0.7
0.5	1.5	0.8	0.8	0.8
0.7	2.0	1.0	1.0	0.9
0.9	2.1	0.6	1.1	0.8
1.5	0.6	----------	1.1	0.3
2.0	0.3	----------	0.8	0.0

The data in the foregoing table indicate that maximum octane appreciation of both RON and MON is obtained with 2-methyl-2,4-pentanediol diacetate at approximately 0.7 to 1.0 volume percent concentration level. With different additives there will be a slight variation in the optimum concentration but in general, optimum results are obtained at concentrations between 0.5 and 1.5 volume percent.

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 a tetraalkyl anti-knock agent, substantial quantities of high octane components selected from the group consisting of olefinic hydrocarbons, aromatic hydrocarbons and mixtures thereof and 2-methyl-2, 4-pentanediol monoacetate in an amount sufficient to improve the octane rating of said hydrocarbon fuel.

2. A hydrocarbon fuel in the gasoline boiling range containing a tetraalkyl anti-knock agent, substantial quantities of high octane components selected from the group consisting of olefinic hydrocarbons, aromatic hydrocarbons and mixtures thereof and pinacol monoacetate in an amount sufficient to improve the octane rating of said hydrocarbon fuel.

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DANIEL E. WYMAN, *Primary Examiner.*

A. D. SULLIVAN, J. GREENWALD, *Examiners.*

Y. H. SMITH, *Assistant Examiner.*