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3,421,867

SATURATED ALIPHATIC HYDROCARBON
GASOLINE

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9 Claims

This application is a continuation of application S.N. 350,650 now abandoned filed on Mar. 10, 1964. This invention relates to hydrocarbon fuel compositions of high octane rating. More specifically, it involves the discovery that the octane rating of leaded saturated aliphatic fuels having a minimum Research Octane Number is substantially improved by the addition of prescribed concentrations of an oxygenated hydrocarbon compound.

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 obtained by the addition of an organo-lead compound decreases as the aromatic and olefin contents of the base fuel increase.

The subject invention is a C-I-P of application S.N. 847,086 filed on Oct. 19, 1959, which is an extension of the discovery that hydrocarbyl monocarboxylic acids, certain derivatives and precursors thereof have an octane appreciating action in leaded fuels having a minimum concentration of aromatics and/or olefin hydrocarbons. In the commonly-assigned copending application Ser. No. 689,466 filed Oct. 11, 1957, by G. W. Eckert, it is disclosed that hydrocarbyl monocarboxylic acids in concentrations of the order of 0.1 to 5.0 volume percent and preferably between 0.2 and 2.0 volume percent, act as octane appreciators in leaded fuels having a minimum aromatic and/or olefinic content of the order of 10 percent. In commonly assigned copending applications Ser. No. 699,944 filed Dec. 2, 1957 and its C-I-P, Ser. No. 743,001 filed June 19, 1958 in the names of G. W. Eckert, and H. V. Hess and E. C. Knowles, it is disclosed that t-alkyl esters of hydrocarbyl monocarboxylic acids in similar concentrations act as octane appreciators in leaded fuels having a minimum aromatic and/or olefinic concentration of the order of 5 percent. In another commonly-assigned copending application Ser. No. 704,303

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filed Dec. 23, 1957 it is disclosed that hydrocarbyl aldehydes in similar concentrations are effective octane appreciators in leaded fuels having a minimum aromatic and/or olefinic content since they apparently are oxidized to hydrocarbyl monocarboxylic acids under the conditions existing in the engine during combustion of the fuel. It has now been discovered that hydrocarbyl monocarboxylic acids, t-alkyl esters thereof and aldehydes are effective octane appreciators in leaded fuels consisting essentially of saturated aliphatic hydrocarbons provided the mixture of leaded saturated paraffinic hydrocarbons has a minimum Research Octane Number (RON).

The high octane hydrocarbon motor fuel of this invention consists essentially of saturated aliphatic hydrocarbons, an organo-lead anti-knock agent, said saturated aliphatic hydrocarbons having a minimum RON with 3 cc. of tetraethyl lead (TEL) per gallon of 102, and 0.1-2.0 volume percent of an oxygenated hydrocarbon which is either a hydrocarbyl monocarboxylic acid containing 1-30 carbon atoms, a t-alkyl ester of said hydrocarbyl monocarboxylic acid, or a hydrocarbyl aldehyde containing 2-30 carbon atoms. When employed in the prescribed concentration and particularly when employed in concentrations between 0.2 and 1.5 volume percent, hydrocarbyl monocarboxylic acids, t-alkyl esters thereof and hydrocarbyl aldehydes substantially improve the carbon fuel having the prescribed minimum RON with 3 cc. of tetraethyl lead per gallon of 102.

Similarly to their octane appreciating action in leaded fuels of minimum aromatic and/or olefinic content which forms the subject matter of the previously-identified copending applications, monocarboxylic acids, t-alkyl esters and aldehydes are ineffective in raising the octane rating of a saturated aliphatic hydrocarbon fuel of minimum RON in the absence of the organo-lead anti-knock agent which is normally TEL. The presence of lead is a requisite for the octane appreciating action of these agents, which fact definitely proves that these agents in raising the octane rating of the saturated paraffinic fuel of minimum octane number are not acting as blending agents. As a matter of fact, the presence of these agents in unleaded fuels in the concentrations above those prescribed herein actually slightly degrades the octane rating of a clear, i.e. unleaded saturated aliphatic hydrocarbon fuel such as alkylate.

A second unusual characteristics of the action of monocarboxylic acids, t-alkyl esters thereof and aldehydes in appreciating the octane rating of saturated aliphatic hydrocarbon fuels in their ineffectiveness in such fuels having an RON rating with 3 cc. of lead per gallon below the prescribed minimum of 102. The reason for the ineffectiveness of these agents in saturated paraffinic fuels of octane rating below the prescribed minimum and their effectiveness in such fuels above the prescribed octane level is currently the subject of intensive investigation but to date must be classified in the realm of the unsolved.

Another unusual feature of the octane appreciating action of monocarboxylic acids, t-alkyl esters and aldehydes in saturated aliphatic hydrocarbon fuels of minimum RON is the fact that the octane appreciating action is apparently restricted to the Research Octane No. These agents do not raise the Motor Octane No. of saturated aliphatic hydrocarbon fuels having Research Octane Numbers substantially above 102 with 3 cc. of TEL per gallon. In this respect, the action of these agents differs from their action in leaded fuels containing a minimum aromatic and/or olefin content of about 5.0 volume percent since in such fuels these agents have an approximately equivalent appreciating action on both the Research and Motor Octane Numbers.

The organo-lead reagent necessary for the action of

monocarboxylic acids, t-alkyl esters and aldehydes 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, tetra-butyl lead, tetraamyl lead, tetrapropyl lead, etc., possess anti-knock properties and may be used in the fuel compositions of the invention.

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 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 4 cc. 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 cc. per gallon in automotive gasoline and 2 to 4.6 cc. per gallon in aviation gasoline. An octane appreciating action is obtained with acid, t-alkyl esters and aldehydes at concentration of 6 cc. TEL per gallon and higher.

The hydrocarbyl monocarboxylic acids and their t-alkyl esters effective in raising the octane rating of leaded saturated gasoline hydrocarbons having a minimum RON of 102 with 3 cc. TEL per gallon are represented by the general formula: RCOOR' wherein R is hydrogen or a hydrocarbyl radical containing 1-29 and preferably 1 to 7 carbon atoms and R' is hydrogen or tertiary aliphatic hydrocarbyl radical of 4-18 and preferably 4 to 12 carbon atoms.

The hydrocarbyl monocarboxylic acid can be aliphatic, cycloaliphatic or aromatic in nature. Examples of effective monocarboxylic acids are the following: acetic acid, propionic acid, 2-ethylhexanoic acid, stearic acid, cumic acid, benzoic acid, cyclohexane carboxylic acid and phenylacetic acid. In general, the most effective monocarboxylic acids are aliphatic and aryl acids containing between 2 and 8 carbon atoms per molecule; the preferred acids accordingly are acetic acid, propionic acid, benzoic acid, pentanoic acid and 2-ethylhexanoic acid.

Tertiary alkyl esters, which are the preferred octane appreciators for commercial use because of their ready preparation from available raw materials and their non-corrosive nature, are exemplified by the following: t-butyl acetate, t-butyl propionate, t-amyl propionate, t-amyl acetate, t-butyl benzoate, t-butyl 2-ethylhexanoate, t-octyl acetate and t-dodecylpropionate. The preferred t-alkyl esters are derived from aliphatic and aromatic monocarboxylic acids containing 2-8 carbon atoms and a tertiary aliphatic hydrocarbyl radical containing 4-12 carbon atoms.

Aldehydes effective in raising the octane rating of leaded saturated aliphatic hydrocarbon gasoline having an RON of at least 102 when leaded with 3 cc. of TEL per gallon are represented by the formula: RCHO wherein R is a hydrocarbyl radical containing 1-29 and preferably 1 to 7 carbon atoms. Preferred aldehydes are those containing 2-8 carbon atoms, i.e. those aldehydes wherein R in the above formula denotes a hydrocarbyl radical containing 1-7 carbon atoms. Examples of effective aldehydes are the following: propionaldehyde, benzaldehyde, n-butyraldehyde, isobutyraldehyde, acetaldehyde, and paraldehyde, the trimer of acetaldehyde.

The octane appreciators must be present in a leaded saturated aliphatic hydrocarbon fuel having a minimum prescribed RON in a concentration of at least 0.1 volume percent before any significant octane appreciation is real-

ized. The most effective concentration of octane appreciator varies with the lead content of the fuel but generally falls in the range between 0.2 and 1.5 volume percent with maximum results normally being obtained between 0.5 and 1.0 volume percent. The upper limit of octane appreciator concentration is placed at 2.0 volume percent both because of economic considerations and because the octane appreciating action of monocarboxylic acids, t-alkyl esters and aldehydes tends to disappear at about this concentration level. The amount of octane appreciation realized with these agents decreases as their concentration exceeds the 1.5 volume percent concentration level.

The action of monocarboxylic acids, t-alkyl esters and aldehydes in saturated aliphatic hydrocarbon fuels having a minimum RON of 102 when leaded with 3 cc. of TEL per gallon is shown in Table I. The base fuel employed in Table I is an isobutylene-isobutane alkylate fraction which when leaded with 3 cc. of TEL per gallon had an RON of 106.2 and an MON of 106.0. This base fuel had an olefin plus aromatic content by Fluorescent Indicator Analysis (FIA) less than 1 percent.

TABLE I.—IMPROVEMENT IN RON AND MON OF LEADED ALKYLATE 106+ RON LEVEL

	Increase in—	
	RON	MON
Base fuel +0.75 v. percent t-butyl acetate.....	0.9	0.0
Base fuel +0.3 v. percent propionic acid.....	0.7	-----
Base fuel +1.0 v. percent isobutyraldehyde.....	0.6	-----
Base fuel +0.75 v. percent t-butyl propionate.....	0.7	-----

The data in the above table indicate that monocarboxylic acids, t-alkyl esters and aldehydes have a significant octane appreciating action on the RON of saturated aliphatic hydrocarbon fuels having the prescribed minimum leaded RON. It is significant that the same improvement was not noted in the MON of the leaded alkylate fuel on addition of t-butyl acetate. This phenomenon, that is, the increase in RON without a corresponding increase in MON is unique with saturated aliphatic hydrocarbon gasolines. These agents effect substantially equivalent increases in the RON and MON ratings of leaded gasoline containing an aromatic and/or olefin content above 5 volume percent.

The critical nature of the upper concentration limit of 2.0 volume percent for the action of tertiary alkyl esters in improving the Research Octane Number of a leaded gasoline consisting essentially of saturated aliphatic hydrocarbons and having a minimum RON of 102 with 3 cc. of TEL per gallon is established by the data in the following table showing that 3, 4 and 5 volume percent of t-butyl acetate in leaded aviation alkylate actually decreased the Research Octane Number of the base fuel. The base fuel employed in obtaining this data was an isobutane-butylene alkylate fraction containing 3 cc. of TEL per gallon and having an RON of 106.8. This base fuel was essentially the same as that employed in Table I above which had an olefin plus aromatic content by Fluorescent Indicator Analysis less than 1%.

EFFECT OF t-BUTYL ACETATE CONCENTRATIONS ABOVE 2 VOLUME PERCENT IN AVIATION ALKYLATE CONTAINING 3 CC. OF TEL PER GALLON AND HAVING AN RON OF 106.8

Percent of t-butyl acetate in base fuel:	Change in RON
3 -----	-2.8
4 -----	-3.9
5 -----	-4.0

In Table II there is demonstrated the ineffectiveness of monocarboxylic acid, t-alkyl esters thereof and aldehydes in raising the octane rating of saturated aliphatic hydrocarbon fuels having an RON below the minimum of 102 when containing 3 cc. of TEL per gallon. Base Fuel A employed in Table II consisted essentially of 2,4-dimeth-

ylpentane and had an RON of 97.8 with 3 cc. of TEL per gallon. Base Fuel B was a light straight run naphtha having a boiling point range of 94–207° F. and an RON of 86.8 with 3 cc. of TEL per gallon.

TABLE II.—ACTION OF OCTANE APPRECIATORS IN SATURATED ALIPHATIC HYDROCARBON FUELS HAVING AN RON BELOW 102 WITH 3 CC. TEL PER GALLON

	Increase in RON
Base Fuel A+0.5 v. percent 2-ethylhexanoic acid---	0.0
Base Fuel B+0.5 v. percent 2-ethylhexanoic acid---	0.0

The data in Table II show the ineffectiveness of hydrocarbyl monocarboxylic acids in raising the octane rating of saturated aliphatic hydrocarbon fuels whose RON with 3 cc. of TEL per gallon is less than 102. Although data on MON is not shown, there was no increase in MON by the addition of the octane appreciators to saturated aliphatic hydrocarbon fuels of the type shown above.

In Table III there are presented data demonstrating the fact that an RON with 3 cc. of TEL per gallon of 102 is the critical minimum required for monocarboxylic acids, t-alkyl esters thereof and aldehydes to act as octane appreciators in leaded saturated aliphatic hydrocarbon fuels. The data presented in Table III show clearly that an RON with 3 cc. TEL per gallon of 102 provides a line of demarcation between the effectiveness and ineffectiveness of the prescribed octane appreciators in improving the RON of saturated aliphatic hydrocarbon fuels.

Base Fuel C employed in Table III was a blend comprising 90% isobutane-isobutylene alkylate and 10% of n-heptane and had an RON of 98.7 and an MON of 101.9 with 3 cc. of TEL per gallon. FIA indicated that this fuel had an aromatic plus olefin content less than 1%.

Base Fuel D employed in Table III comprised 84% isobutane-isobutylene alkylate and 16% n-heptane and had an RON of 98.0 and an MON of 101.4 with 3 cc. TEL per gallon. FIA analysis indicated that this fuel had an aromatic plus olefin content less than 1%.

Base Fuel E was a blend comprising 91% isobutane-isobutylene alkylate and 9% Udex raffinate and had an RON of 102 and an MON of 103.3 with 3 cc. TEL per gallon. FIA showed that the aromatic plus olefin content of this fuel was less than 1 volume percent. Udex raffinate is a residual fraction obtained in diethylene glycol extraction of catalytic reformat.

Base Fuel F is a blend of 95% isobutane-isobutylene alkylate and 5% Udex raffinate and had an RON of 103.5 and an MON of 106.0 with 3 cc. of TEL per gallon. FIA indicated that the aromatic plus olefin content of this fuel was less than 1 volume percent.

The results of adding 0.75% of t-butyl acetate to these various base fuels is shown in Table III.

TABLE III.—EFFECT OF t-BUTYL ACETATE ON THE RON AND MON OF SATURATED ALIPHATIC HYDROCARBON FUELS

	Increase	
	RON	MON
Base fuel C (RON 98.6)+0.75 v. percent t-butyl acetate	-0.1	-0.1
Base fuel D (RON 98.0)+0.75 v. percent t-butyl acetate	0.0	0.0
Base fuel E (RON 102.0)+0.75 v. percent t-butyl acetate	+0.2	-0.3
Base fuel F (RON 103.5)+0.75 v. percent t-butyl acetate	+0.2	-0.4

The data in the above table clearly demonstrate the critical nature of the prescribed RON with 3 cc. TEL per gallon of 102 for the action of t-butyl acetate in improving the RON of saturated aliphatic hydrocarbon fuels. The data in the above table also show that t-butyl acetate does not improve the MON of saturated aliphatic hydrocarbon fuels both above and below the prescribed 102 RON minimum.

As with the aromatic and/or olefinic leaded fuels, monocarboxylic acids, t-alkyl esters and aldehydes become more

effective in saturated aliphatic hydrocarbon fuels as the octane level rises. This is shown in Table IV demonstrating the action of t-butyl acetate in a concentration of 0.75 volume percent in an isobutane-isobutylene alkylate fraction having an RON of 108.7 and an MON of 107.6 with 3 cc. of TEL per gallon.

TABLE IV.—ACTION OF t-BUTYL ACETATE IN AN ALKYLATE HAVING 108.7 RON WITH 3 CC. TEL PER GALLON

Base Fuel+0.75 v. percent t-butyl acetate (increase):	
RON -----	1.6
MON -----	0.0

A comparison of the 1.6 RON improvement obtained by the presence of 0.75 volume percent t-butyl acetate in the 108.7 RON leaded alkylate in the above table with the 0.7 unit improvement obtained with the same concentration of t-butyl acetate in the 106.2 RON leaded alkylate of Table I shows the increasing effectiveness of the octane appreciators in saturated aliphatic hydrocarbon fuels as the RON of the base fuel exceeds the minimum level of 102.

The data in Table V show the octane appreciating action of acids and t-alkyl esters on the RON of a leaded paraffinic reference fuel comprising 10% isopentane, 5% n-heptane and 85% isooctane and having an RON of 104.9 and an MON of 110.3 with 3 cc. of TEL per gallon.

TABLE V.—ACTION OF ACIDS AND t-ALKYL ESTERS IN SATURATED ALIPHATIC HYDROCARBON REFERENCE FUEL CONTAINING 3 CC. TEL PER GALLON

	Increase in RON
Reference Fuel+0.5% benzoic acid -----	0.4
Reference Fuel+1.0% benzoic acid -----	0.5
Reference Fuel+0.75% t-butyl acetate -----	+0.3
Reference Fuel+0.75% t-butyl propionate -----	+0.3

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 consisting essentially of saturated aliphatic hydrocarbons having a minimum research octane number with 3 cc. of tetraethyl lead per gallon of 102, said fuel containing an organo-lead anti-knock agent in a concentration of at least 0.5 cc. per gallon and 0.1 to 2.0 volume percent of an oxygenated hydrocarbon selected from the group consisting of t-alkyl esters of a hydrocarbyl monocarboxylic acid, said monocarboxylic acids containing from 1 to 30 carbon atoms, said concentration of said oxygenated hydrocarbons effecting a substantial improvement in the research octane number of said saturated aliphatic hydrocarbon fuel.

2. A hydrocarbon fuel according to claim 1 in which said oxygenated hydrocarbon is present in a concentration between 0.2 and 1.5 volume percent.

3. 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.

4. A hydrocarbon fuel according to claim 1 in which said esters have the general formula:



in which R is selected from the group consisting of hydrogen and hydrocarbyl radicals containing 1 to 29 carbon atoms and R' is selected from the group consisting of a tertiary aliphatic hydrocarbon radical containing 4 to 18 carbon atoms.

5. A hydrocarbon fuel in the gasoline boiling range consisting essentially of saturated aliphatic hydrocarbons hav-

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ing a minimum RON with 3 cc. of tetraethyl lead per gallon of 102, said fuel containing an alkyllead anti-knock agent in a concentration of at least 0.5 cc. per gallon and 0.1 to 2.0 volume percent of an oxygenated hydrocarbon selected from the group consisting of oxygenated hydrocarbons of the general formula:



wherein R is a hydrocarbon radical containing 1 to 7 carbon atoms per molecule and R' is a tertiary aliphatic hydrocarbon radical containing 4 to 12 carbon atoms, said concentration of said oxygenated hydrocarbon effecting a substantial improvement in the research octane number of said saturated aliphatic hydrocarbon fuel.

6. A hydrocarbon fuel according to claim 5 in which the concentration of oxygenated hydrocarbon is between 0.2 and 1.5 volume percent.

7. A hydrocarbon fuel according to claim 5 containing 1.0 to 4.6 cc. of tetraethyl lead per gallon.

8. A hydrocarbon fuel according to claim 5 in which said oxygenated hydrocarbon is t-butyl acetate.

9. A hydrocarbon fuel according to claim 5 in which said oxygenated hydrocarbon is t-butyl propionate.

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