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 anhydrides of monocarboxylic acids.

The recent increases in compression ratios of automotive engines have placed a severe strain on petroleum refineries 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 organolead 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 organolead 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 anhydrides of monocarboxylic acids.

In copending application Ser. No. 689,466, filed Oct. 11, 1957, it is disclosed that monocarboxylic acids substantially raise the octane rating of a motor fuel containing an organolead 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 anhydrides of monocarboxylic acids exert a similar anti-knock action in motor fuel compositions of the present 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, organolead anti-knock agent and an anhydride of a monocarboxylic acid in a concentration of at least 0.1 volume percent of the fuel.

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

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

The third unusual feature of the action of anhydrides of monocarboxylic acids 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 organolead anti-knock agent is present. Since organolead 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. Anhydrides of monocarboxylic acids 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. The minimum 5 percent concentration is necessary for anhydrides of monocarboxylic acids 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 organolead reagent necessary for the action of anhydrides of monocarboxylic acids 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 tetrasmethyl lead, tetrabutyl lead, tetramethyl lead, tetrapropyl lead, etc., possess anti-knock properties and may be used in the fuel compositions of the invention in conjunction with anhydrides of monocarboxylic acids.

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, "tetaethyl lead fluid" denotes the commercial product which comprises tetraethyl lead, ethylene chloride and ethylene bromide, the latter two reagents being present in the 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 organolead reagent is present in the fuel compositions of the invention in concentrations between 0.5 ml. per gallon up to the statutory limit of organolead 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.
The acid anhydrides of monocarboxylic acids which are effective in increasing the octane rating of an aromatic and/or olefin-containing gasoline in the presence of an organo-lead antiknock agent have the general formula:

\[ R\text{-}C\text{O}\text{-}O\text{-}C\text{O}-R' \]

wherein R and R' are hydrocarbyl radicals containing 1-29 carbon atoms. Usually, the R and R' are identical radicals but mixed anhydrides wherein the R and R' are dissimilar radicals may also be used in the motor fuels of the invention. Anhydrides derived from aliphatic monocarboxylic acids, cycloaliphatic monocarboxylic acids, and aromatic monocarboxylic acids are effective as octane appreciators in leaded fuels containing the prescribed aromatic and/or olefin content. Acid anhydrides effective as octane appreciators in the fuel compositions of the invention are exemplified by the following:

- Acetic anhydride, propionic acid anhydride, n-butyl ester anhydride, isobutyric acid anhydride, heptanoic acid anhydride, lauric acid anhydride, myristic acid anhydride, palmitic acid anhydride, o-cumene acid anhydride, benzoic acid anhydride, cyclohexane carboxylic acid anhydride, cinnamic acid anhydride, phenyl acetic acid anhydride, and toluic acid anhydride.

The preferred acid anhydrides used in the fuel compositions of the invention are derived from aliphatic and aromatic monocarboxylic acids containing 1-14 carbon atoms. Particularly preferred acid anhydrides are acetic acid anhydride, propionic acid anhydride, n-butyl ester anhydride, benzoic acid anhydride, 2-ethylhexanoic acid anhydride, and isocaproic acid anhydride.

The anhydrides of monocarboxylic acids 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 improvement is realized. When the concentration of monocarboxylic acid anhydride 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 monocarboxylic acid anhydride in the fuel compositions of the invention fall between 0.2 and 2.0 volume percent with maximum octane improvement generally being obtained at a concentration level of about 0.5 volume percent. Concentrations of anhydrides of monocarboxylic acids as high as 5 volume percent can be incorporated in the fuel compositions but no additional octane improvement is realized at the higher concentrations and economic considerations preclude the use of such concentrations in commercial fuel compositions.

In Table I there is shown the effectiveness of anhydrides of monocarboxylic acids in raising the octane rating of a leaded fuel composition containing prescribed aromatic and/or olefin content. The base fuel employed in Table I contained 3 cc. of tetraethyl lead fluid (TEL) per gallon and had an octane rating of 101.3; it comprised approximately 7.1 percent butane, 62.3 percent catalytically reformed naphtha, and 30.6 percent light fluid catalytically cracked naphtha. The aromatic content of this leaded fuel was 46 percent as measured by the Fluorescent Indicator Analysis (FIA) Method and its boiling point range was 90 to 351° F.

### Table I - Effect of Anhydrides on Research Octane Ratings of 101.3 Octane Gasoline

<table>
<thead>
<tr>
<th>Anhydride</th>
<th>Volume percent of anhydride in fuel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic anhydride</td>
<td>0.1  0.25  0.5  0.75  1.0  1.5</td>
</tr>
<tr>
<td>Proponic acid anhydride</td>
<td>0.1  0.25  0.5  0.75  1.0  1.5</td>
</tr>
<tr>
<td>Butyric acid anhydride</td>
<td>0.1  0.25  0.5  0.75  1.0  1.5</td>
</tr>
<tr>
<td>Isobutyric acid anhydride</td>
<td>0.1  0.25  0.5  0.75  1.0  1.5</td>
</tr>
</tbody>
</table>

The data in the above table demonstrate that substantial improvements in octane rating result from the incorporation of acid anhydrides in 105 octane gasoline containing lead and the prescribed aromatic and/or olefin content. It is significant that a larger octane improve-ment is obtained at the 105 octane level than at the 100 octane level by the incorporation of equivalent amounts of additive. This fact can be ascertained by a comparison of the improvements resulting from the incorporation of 0.5 and 0.75 volume percent anhydride in the 105 octane gasoline with the improvements obtained by the equivalent amounts of anhydrides in the 101.3 octane gasoline.

This invention also contemplates a process for operating a spark ignition internal combustion engine involving the use of a leaded fuel of the prescribed aromatic and/or olefin content and separate introduction of measured quantities of anhydrides of monocarboxylic acids into the combustion zone to give a concentration of anhydride of at least 0.1 volume percent of the total fuel in the combustion zone. Auxiliary fuel systems which have been used for water injection into fuels operating under load conditions can be readily converted to this type of operation wherein measured quantities of anhydrides are introduced into the combustion zone. This process is particularly applicable to the operation of engines having a compression ratio above 7.5.

Obviously, many modifications and variations of the invention as hereinafter 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 lead antiknock agent, at least 5 volume percent of high octane components selected from the group consisting of olefinic hydrocarbons, aromatic hydrocarbons, and mixture thereof and an anhydride of a gasoline-soluble saturated hydrocarbyl monocarboxylic acid in an amount sufficient to further improve the octane rating of said hydrocarbon fuel.

2. A hydrocarbon fuel in the gasoline boiling range containing an organo-lead antiknock agent, 5.0 volume percent of high octane components selected from the group consisting of olefinic hydrocarbons, aromatic hydrocarbons and mixtures thereof and an anhydride of hydrocarbyl monocarboxylic acids containing up to 50 carbon atoms 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 hydrocarbon fuel.
5 3. A hydrocarbon fuel according to claim 2 in which the monocarboxylic acid anhydride has the general formula:

\[
\overset{0}{R} \overset{0}{-} \overset{}{O} \overset{}{\overset{0}{C}} \overset{}{\overset{0}{-}} \overset{}{O} \overset{}{R'}
\]

in which \( R \) and \( R' \) are hydrocarbyl radicals containing 1–29 carbon atoms.

4. A hydrocarbon fuel according to claim 2 in which said organo-lead antiknock agent is present in a concentration between 0.5 and 4.6 cc. per gallon.

5. A hydrocarbon fuel in the gasoline boiling range containing an alkyl lead antiknock 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 volume percent of said fuel and an anhydride of a monocarboxylic acid having the general formula:

\[
\overset{0}{R} \overset{}{\overset{0}{C}} \overset{}{\overset{0}{-}} \overset{}{O} \overset{}{\overset{0}{C}} \overset{}{\overset{0}{-}} \overset{}{O} \overset{}{R'}
\]

in which \( R \) and \( R' \) are hydrocarbyl radicals containing 1–29 carbon atoms in a concentration of 0.1 to 5.0 volume percent.

6. A hydrocarbon fuel according to claim 5 in which the concentration of said anhydride is between 0.2 and 2.0 volume percent.

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

8. A hydrocarbon fuel according to claim 5 containing 1.0–4.6 cc. TEL per gallon.

9. A hydrocarbon fuel according to claim 5 in which said anhydride is acetic anhydride.

10. A hydrocarbon fuel according to claim 5 in which said anhydride is propionic acid anhydride.

11. A hydrocarbon fuel according to claim 5 in which said anhydride is n-butyric acid anhydride.

12. A hydrocarbon fuel according to claim 5 in which said anhydride is isobutyric acid anhydride.

13. A process for operating a spark ignition internal combustion engine having a compression ratio above about 7.5 which comprises charging to the combustion zone a gasoline fuel comprising high octane components selected from the group consisting of olefinic hydrocarbons, aromatic hydrocarbons and mixtures thereof in a concentration of at least 5 volume percent of said fuel and an organo-lead antiknock agent and separately introducing into said combustion zone measured amounts of an anhydride of monocarboxylic acids of the general formula:

\[
\overset{0}{R} \overset{}{\overset{0}{C}} \overset{}{\overset{0}{-}} \overset{}{O} \overset{}{\overset{0}{C}} \overset{}{\overset{0}{-}} \overset{}{O} \overset{}{R'}
\]

References Cited

UNITED STATES PATENTS

1,692,784 11/1928 Orelup et al. ------- 44—66
2,528,605 11/1950 Partridge et al. ------- 44—69
2,360,585 10/1944 Ross et al. ------- 44—80

FOREIGN PATENTS

640,311 7/1928 France.

OTHER REFERENCES


DANIEL E. WYMAN, Primary Examiner.

Y. H. SMITH, Assistant Examiner.

U.S. Cl. X.R.