

1

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MOTOR FUEL CONTAINING AN OCTANE APPRECIATOR

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This invention relates to a motor fuel composition of high octane rating containing a novel octane appreciator. More particularly, the invention relates to a motor fuel composition for spark ignition, internal combustion engines containing an hydroxypyridine as an effective octane appreciator for leaded gasolines.

Increases in the compression ratios of spark-ignited, internal combustion engines for modern automobiles places a severe strain on petroleum refiners' ability to produce fuels having the octane rating demanded by these engines. At the present time, premium fuels have research octane numbers in the order of 100. It is predicted that the research octane number of premium fuels will have to be raised to 105 or more in the future in order to satisfy the octane requirements for a new generation of high compression automobile engines.

At the present time refiners rely heavily on catalytic refining operations, such as fluid catalytic cracking, catalytic reforming, alkylation and catalytic isomerization to produce high octane gasoline. Catalytic cracking and catalytic reforming, the most widely used refining operations for the production of high octane fuels, produce substantial quantities of aromatics. Catalytic cracking, in addition, produces a substantial amount of olefins. While olefins and aromatics have high octane ratings, they exhibit poor response to the organo-lead octane improving compounds, such as tetraethyl lead. This behavior is in contrast to the behavior of saturated aliphatic gasoline components which exhibit a good lead response. Accordingly, as the aromatic and olefinic content of gasoline has been increased to meet the octane levels required by high compression engines, the lead response of the resulting fuels has diminished. In other words, the incremental octane improvement obtainable by the addition of an organo-lead compound decreases as the aromatic and olefinic content of the base fuel is increased.

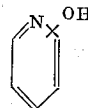
The present invention involves the discovery that a high octane gasoline fuel can be substantially improved with respect to its research octane number by the addition thereto of a hydroxy-substituted pyridine. Since hydroxypyridines have poor solubility in gasoline, it is necessary to employ a solubility promoter, e.g. an alcohol, to promote the solubility of the hydroxypyridine in the gasoline to realize the improvement in octane rating. The improvement in octane value is only exhibited by gasolines containing a tetraalkyl lead anti-knock compound, non-leaded gasolines exhibit no improvement due to the addition of a hydroxypyridine.

The high octane motor fuel composition of the invention comprises a mixture of hydrocarbons in the gasoline boiling range containing an effective anti-knock amount of a tetraalkyl lead fluid, 0.01 to 5 volume percent of a hydroxy-substituted pyridine, and a solubility promoter effective for promoting the solubility of the hydroxypyridine in gasoline. Alcohols represented by the formula: ROH in which R is a radical selected from the group consisting of aliphatic and cycloaliphatic hydrocarbyl radicals having from 1 to 24 carbon atoms are effective solubility promoters for gasoline.

The essential octane appreciator component of the in-

2

vention is a hydroxypyridine corresponding to the formula:



The formula is representative of the hydroxypyridine species, namely, 2-hydroxypyridine, 3-hydroxypyridine and 4-hydroxypyridine. These compounds have relatively poor solubility in gasoline and a solubility promoter must be employed in conjunction with the hydroxypyridine to make them sufficiently soluble to realize an improvement in the research octane number of gasoline. The hydroxypyridine is employed in amounts ranging from about 0.01 to 5 volume percent with the preferred amounts being from 0.1 to 2 percent.

Alcohols corresponding to the formula: ROH in which R is an aliphatic or cycloaliphatic hydrocarbyl radical having from 1 to 24 carbon atoms are effective solubility promoters for hydroxypyridines. Specific alcohols which can be employed include methyl alcohol, ethyl alcohol, isopropyl alcohol, tertiary-butyl alcohol, n-amyl alcohol, isoamyl alcohol, n-hexyl alcohol, cyclohexanol, 2,2-dimethyl-1-hexanol, oleyl alcohol, lauryl alcohol, and the like. The alcohols are effective in concentrations ranging from about 0.1 to 10 volume percent with the preferred concentration being from about 0.5 to 5 percent.

It has been found preferable to mix the hydroxypyridine with the aliphatic or cycloaliphatic alcohol prior to adding the mixture to the gasoline composition. Premixing these components greatly facilitates the solubility of the hydroxypyridine in gasoline. The advantage of the invention may be obtained, however, by separately adding the hydroxypyridine and the alcohol to gasoline although a longer period of time will be required to effect complete solubility of the hydroxypyridine.

It is essential to this invention that the gasoline be a leaded gasoline, that is a gasoline composition containing a tetraalkyl lead, anti-knock mixture. Hydroxypyridines give no improvement when added to a base fuel containing no tetraalkyl lead component.

The tetraalkyl lead compounds commonly employed are tetraethyl lead, tetramethyl lead and mixtures of same. As commercially supplied for automotive use, the tetraalkyl lead is supplied in admixture with an ethylene chloride-ethylene bromide mixture which acts as the scavenger for removing the lead from the combustion chamber in the form of volatile lead halides. Tetraethyl lead fluid is the commercial product which comprises tetraethyl lead, ethylene chloride and ethylene bromide, the latter two compounds being present in 1.0 theory and 0.5 theory, respectively, denoting the stoichiometric amount required for use with the lead content of the tetraethyl lead. The gasoline of the invention will ordinarily contain from 0.5 to 4.5 cc. per gallon of tetraethyl lead fluid.

The base fuel of the invention consists of a mixture of hydrocarbons boiling in the gasoline boiling range, that is, boiling in the range from about 90 up to about 425° F. The gasoline may be a straight run gasoline or it may be obtained by catalytic-cracking, catalytic-reforming, alkylation or polymerization and may comprise substantial amounts of aliphatic, aromatic and olefinic hydrocarbons in the gasoline boiling range.

The effectiveness of hydroxypyridines as octane appreciators for a leaded gasoline composition is shown in the examples below. The base fuel employed in these tests was a premium gasoline having a research octane number of 101 and containing 3 cc. of tetraethyl lead mix per gallon. The base fuel consisted of 35.5 percent

aromatics, 9.5 percent olefins and 55 percent aliphatic hydrocarbons as determined by FIA analysis and had an initial boiling point of 94° F. and an end point of 370° F.

TABLE I.—RESEARCH OCTANE INCREASE OF GASOLINE WITH HYDROXYPYRIDINE AND VARIOUS ALCOHOLS

Hydroxypyridine, percent vol.	Alcohol and percent vol. in gasoline ¹	Δ RON ²
2-hydroxypyridine 0.50.....	Methyl alcohol 2.0.....	+1.0
Do.....	Isopropyl alcohol 2.0.....	+0.5
Do.....	t-Butyl alcohol 2.0.....	+0.8
Do.....	n-Amyl alcohol 2.0.....	+0.7
Do.....	iso-amyl alcohol 2.0.....	+0.3
Do.....	n-Hexyl alcohol 2.0.....	+0.5
Do.....	Cyclohexanol 2.0.....	+0.5
Do.....	2,2-dimethyl-1-hexanol 0.5....	+0.5
Do.....	Oleyl alcohol 2.0.....	+0.2
3-hydroxypyridine 0.50.....	Methyl alcohol 5.0.....	+0.5

¹ The alcohol and 2-hydroxypyridine were premixed before addition to the gasoline.

² The Δ RON is the difference between the octane number of the fuel containing hydroxypyridine and alcohol and that of the fuel containing only the alcohol. A plus value indicates an increase in octane value caused by the hydroxypyridine.

TABLE II.—COMPARISON OF 2-HYDROXYPYRIDINE IN LEADED AND UNLEADED GASOLINES

2-hydroxypyridine, ¹ percent vol.	Methyl alcohol, ¹ percent vol.	Δ RON base fuel 3 cc. TEL mix in gasoline	Δ RON ² unleaded gasoline
0.10.....	1.0	+0.1	-0.2
0.20.....	1.0	+0.3	-0.2
0.30.....	1.0	+0.4	-0.0
0.40.....	1.0	+0.5	-0.0
0.50.....	1.0	+0.7	-0.0
0.60.....	1.0	+0.7	-0.0
0.70.....	1.0	+0.7	-0.0

¹ Methyl alcohol and 2-hydroxypyridine premixed before addition to the fuel.

² See footnote 2 Table I.

TABLE III.—EFFECT OF CONCENTRATION OF 2-HYDROXYPYRIDINE ON RESEARCH OCTANE NUMBER OF GASOLINE

2-hydroxypyridine, ¹ percent vol.	Methyl alcohol, percent vol.	Δ RON ²
0.1.....	2.0	+0.1
0.3.....	2.0	+0.3
0.4.....	2.0	+0.5
0.5.....	2.0	+1.0
0.6.....	2.0	+0.6
0.7.....	2.0	+0.4
0.8.....	2.0	+0.3
0.9.....	2.0	+0.2
1.0.....	2.0	+0.3

¹ Additives premixed.

² See footnote 2 Table I.

TABLE IV.—EFFECT OF COMPOUNDS OTHER THAN HYDROXYPYRIDINE IN GASOLINE

Additive ¹	Percent vol.	Methyl alcohol, ¹ percent vol.	Δ RON ²
N-beta-hydroxyethyl pyridine.....	0.50	1.0	-0.10
N-beta-hydroxyethyl morpholine....	0.50	0.5	0.0
1-diethylamino-2-propanol.....	0.30	-----	0.0
Beta-hydroxyethyl aniline.....	1.0	2.0	0.0

¹ Additives premixed.

² See footnote 2 Table I.

The foregoing examples illustrate the remarkable effectiveness of hydroxypyridines for enhancing the re-

search octane number of a high octane leaded gasoline composition. It is understood that the gasoline of the invention can contain conventional motor fuel additives, such as anti-stalling agents, stabilizers, corrosion inhibitors, deposit modifiers and the like.

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.

I claim:

1. A motor fuel composition comprising a mixture of hydrocarbons in the gasoline boiling range containing an effective anti-knock amount of a tetraalkyl lead fluid, 0.05 to 5 volume percent of hydroxy-substituted pyridine selected from the group consisting of 2-hydroxypyridine, 3-hydroxypyridine and 4-hydroxypyridine and a solubility promoter effective to promote the solubility of said hydroxypyridine in said composition.

2. A composition according to claim 1 in which said solubility promoter is an alcohol represented by the formula:



in which R is a radical selected from the group consisting of aliphatic and cyclo-aliphatic radicals having from 1 to 24 carbon atoms.

3. A composition according to claim 2 containing from 0.5 to 4.5 cc. of a tetraalkyl lead fluid per gallon and from 0.1 to 10 weight percent of said solubility promoter.

4. A motor fuel composition according to claim 1 in which said pyridine is 2-hydroxypyridine.

5. A motor fuel composition according to claim 1 in which said pyridine is 3-hydroxypyridine.

6. A motor fuel according to claim 2 containing 0.5 to 4.5 cc. of a tetraalkyl lead fluid, 0.1 to 2 volume percent of said hydroxy-substituted pyridine and from 0.5 to 5 volume percent of said alcohol.

7. A composition according to claim 2 in which said solubility promoter is methyl alcohol.

8. A composition according to claim 2 in which said solubility promoter is n-amyl alcohol.

9. A composition according to claim 2 in which said solubility promoter is t-butyl alcohol.

10. A composition according to claim 2 in which said solubility promoter is isopropyl alcohol.

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