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FUEL COMPOSITION

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This invention relates to an improved internal combustion engine fuel. More particularly it pertains to a leaded gasoline containing a specific polyhalogenated hydrocarbon additive which lowers the octane requirement increase and suppresses deposit formation of the engine in which it is used.

Octane requirement increase (ORI) of internal combustion engines is a well known phenomenon in the art. Briefly, it consists of a demand by a new motor for fuels having increasingly higher octane numbers in order to exhibit knock-free operation. The demand for a higher octane fuel ceases when a so-called point of equilibrium is reached at which point the quantity of deposit formation remains substantially even and the octane requirement of the engine remains relatively constant.

The initial build-up of deposits in the combustion chamber of the spark ignition engine may be at least partially caused by the use of organic lead compounds in the fuel to increase the octane number thereof. After ignition some of the lead may remain in the combustion chamber in the form of deleterious deposits which tend to promote surface ignition and increase octane requirement of the engine.

Tetraethyl lead (TEL) is usually incorporated in present day gasoline fuels used commercially for public automotive consumption in amounts of from about 2 to 3 ml. per gallon. Most so-called regular gasoline fuels use in the neighborhood of 2.5+ ml. of TEL per gal. The upper limit of 3 ml. has been designated as the maximum presently allowable amount in automotive fuels. Tetraethyl lead as supplied for automotive use contains 1.0 theory ethylene chloride and about 0.5 theory ethylene bromide. One (1.0) theory, as stated above, designates the theoretical amount of additive required to convert all the lead present in the fuel to the lead halide. These compounds are lead scavengers which serve to remove lead from the combustion chamber in the form of lead chlorides and bromides. The combined tetraethyl lead, ethylene chloride and bromide is usually referred to as the tetraethyl lead (TEL) fluid.

Many compounds, including certain polyhalogenated hydrocarbons, have been proposed as additives for leaded gasoline to lower octane requirement increase. U.S. Patent No. 2,784,160 in particular discloses three compounds which when added to a gasoline containing tetraethyl lead reduce the octane requirement of the engine. The polyhalogenated hydrocarbons disclosed are 1-bromo-1,1-dichloro - 2,2,2 - trifluoroethane ($BrCl_2C—CF_3$), 1,2-dibromo-1-chloro-1,2,2-trifluoroethane

($BrClFC—CF_2Br$)

and 1,1,2,2-tetrachloro-1,2-difluoroethane

($Cl_2FC—CFCl_2$)

To show that these compounds were unexpectedly useful, the patentees disclosed the results of tests on other closely related polyhalogenated hydrocarbons in gasoline which did not display any advantageous results.

In accordance with this invention a superior motor fuel composition for spark ignition engines comprises a major amount of a hydrocarbon boiling within the gasoline range, tetraethyl lead and from 0.1 to 1.0 theory based on the tetraethyl lead of 1,1-difluoro-2,2-dichloro-1,2 dibromo ethane.

The preferred amount of 1,1-difluoro-2,2 dichloro 1,2-dibromo-ethane which is used in the present invention is about 0.5 theory. One (1.0) theory designates the theoretical amount of additive necessary to convert all the lead present in the fuel to the lead halide. Generally, the amount of this additive which is useful in terms of percent by weight based on the total fuel containing from 0.1 to 3 ml. per gal. of tetraethyl lead is from 0.0008 to 0.052 percent.

The base fuel in accordance with this invention is a hydrocarbon fuel boiling within the gasoline range. This includes straight run gasolines, alkylate, thermally and catalytically cracked gasolines, catalytically reformed and hydroformed gasolines and mixtures of these types with themselves and other paraffinic, olefinic and aromatic hydrocarbons to form a suitable fuel.

Other conventional spark ignition motor fuel additives are used in the fuels of the invention to produce fuels suitable for present day high compression, high speed engines, such additives include, rust and oxidation inhibitors, stabilizers, coloring agents, metal deactivators and gum inhibitors.

To demonstrate the very excellent ability of 1,1-difluoro-2,2-dichloro-1,2-dibromoethane to reduce octane requirement increase of a spark ignition engine, the following test procedure was used:

LAUSON H–2 OCTANE REQUIREMENT INCREASE (ORI) TEST PROCEDURE

A modified Model–H–2 Lauson engine, which is a single cylinder, liquid cooled, four stroke spark ignition engine with a bore of 2⅝ inches and a stroke of 2¾ inches giving a displacement of 14.89 cubic inches, was used. Power output was rated at 4.3 H.P. at 2400 r.p.m. Compression ratio of the engine was 6.5:1 using a modified head. The original flywheel magneto was replaced with a Bendix-Scintilla magneto, Type CBR–4R and coupled to the forward end of the crankshaft to provide ignition. The engine was also coupled to a 3 H.P. induction motor to provide the load. The following test operating conditions were observed:

Test duration	To equilibrium O.R. =approx. 200–300 hrs.
Speed, r.p.m.	1750.
Load, B.H.P.	Approx. 2.1.
Spark advance, ° B.T.C.	20.
Fuel flow rate, lbs./hr.	1.6.
Air-fuel ratio	13.5:1.
Coolant temp., ° F.	210.
Carburetor air temp., ° F.	100.
Oil temp., ° F.	175.

The following test procedure was employed:

Octane requirement of the engine was determined with reference fuels on the clean engine and approximately every 24 hours thereafter to equilibrium octane requirement. Equilibrium octane requirement was reached when the engine had operated for 50 hours with a change in ORI of 2 numbers or less. The difference between the initial (clean engine) octane requirement and the equilibrium octane requirement is known as the octane requirement increase or ORI.

Example I

Using the foregoing test procedure, the ORI of a premium reference fuel comprising mainly fluid catalytically

cracked stock and straight run gasoline was developed. This fuel contained 2.9 ml./gal. of tetraethyl lead fluid, and had an ASTM research octane rating of 95.1. The reference fuel had °API gravity of 56.8 and a boiling point range between 103 and 390° F. It was negative in the Copper Corrosion Test and had an oxidation stability in the ASTM test of 840 minutes. This fuel also contained about 6 lbs. per 1000 bbs. of fuel of N,N'-disecondary butyl-p-phenylenediamine, a gum inhibitor, about 1.2 lbs. per 1000 bbs. of fuel of N,N'-disalicylidene-1,2-diaminopropane, a metal deactivator, and about 1.1 lbs. per 1000 bbs. of fuel of lecithin, a fuel stabilizer. The following table shows the data developed during the test procedure:

Table I

LAUSON H-2 ORI TEST RESULTS

Additive:	ORI
None	18
1,1-difluoro-2,2-dichloro-1,2-dibromoethane (0.5 theory)	10
1,2-dibromo-1-chloro - 1,2,2 - trifluoroethane (0.5 theory)	14

The great reduction of ORI by the addition to the leaded fuel of the additive of the invention is very significant. These exceptional results are made even more unexpected when viewed in the light of the test results on the fuel composition containing the additive of the prior art (BrClFC—CF_2Br) which is known to have an ORI reducing effect. The ability of the additive of the invention (BrF_2C—CCl_2Br) to reduce ORI of the fuel appears to be about 100 percent greater than the known prior art additive basis the test data developed.

The compound of the invention also has a cleanliness effect on the test engine. The following table demonstrates this ability. These data were developed during the tests reported in Example I.

Table II

COMBUSTION AREA DEPOSITS IN LAUSON H-2 ENGINE

	Reference fuel	Reference fuel plus additive
Weight, g	16.43	11.41
Volume, cc	5.7	4.3
Density, g./cc	2.88	2.65

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. An improved spark ignition motor fuel comprising a major proportion of a hydrocarbon boiling within the gasoline range, tetraethyl lead, and 1,1-difluoro-2,2-dichloro-1,2-dibromoethane in an amount sufficient to reduce octane requirement increase.

2. An improved spark ignition motor fuel as described in claim 1 containing 0.1 to 1.0 theory 1,1-difluoro-2,2-dichloro-1,2-dibromoethane.

3. An improved spark ignition motor fuel as described in claim 1 containing 0.1 to 3 ml. per gallon of tetraethyl lead.

References Cited in the file of this patent

UNITED STATES PATENTS

2,327,708	Herbst	Aug. 24, 1943
2,784,160	Blaker	Mar. 5, 1957

OTHER REFERENCES

Rounds et al.: "Effects of Halocarbons on Engine Performance," Ind. and Eng. Chem., vol. 46, No. 8, pp. 1677–1684, August 1954.