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TETRAMETHYLLEAD AND ARYLPHOSPHATE GASOLINE COMPOSITION

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3 Claims. (Cl. 44—69)

ABSTRACT OF THE DISCLOSURE

High octane hydrocarbon base gasoline contains at least 20% by volume of aromatic hydrocarbons, tetramethyllead and arylphosphate.

This application is a continuation-in-part of U.S. application Ser. No. 118,503, and now abandoned, filed June 21, 1961, by Maurice R. Barusch, Wallace L. Richardson, George J. Kautsky and Donel R. Olson, which in turn is a continuation-in-part of U.S. application Ser. No. 765,920, filed Sept. 26, 1958, and now U.S. Patent 3,316,071 by Maurice R. Barusch, Wallace L. Richardson, George J. Kautsky and Donel R. Olson.

This invention relates to an improved leaded gasoline composition. More particularly the invention is concerned with a superior new hydrocarbon base fuel boiling in the gasoline boiling range containing lead tetramethyl and aryl phosphate.

Modern gasoline compositions for spark ignition internal combustion engines are commonly characterized by high octane numbers due to the trend toward increased compression ratios. Such high octane numbers are customarily obtained by the selection of suitable hydrocarbon base stocks and the addition of tetraethyllead antidetonant to suppress knock.

Unfortunately it has been generally found heretofore that there is a limit to the improvement in octane number that can be obtained by conventional selection of hydrocarbon base stocks and tetraethyllead. For example, preferred high octane base stocks of substantial aromatic content in combination with tetraethyllead are characterized by a practical maximum octane number beyond which additional increments of tetraethyllead provide less and less octane number improvement.

The use of tetraethyllead antiknock agent in modern spark ignition internal combustion engines has a further disadvantage in that lead containing deposits are formed in the cylinders of the engines. These deposits become hot during the operation of the engines and cause preignition in which the fuel and air mixture commences to burn before the proper time for ignition by the spark plugs. The premature combustion of the mixture in the cylinder is evidenced by a loud knock and results in a serious reduction in power.

It has now been found that a superior new leaded gasoline composition of high octane number for spark ignition internal combustion engines is provided by a hydrocarbon base fuel boiling in the gasoline boiling range having a clear Research octane number of at least 90 and containing at least 20% by volume of aromatic hydrocarbons, said fuel containing a minor proportion of tetramethyllead in an amount sufficient to improve the octane number, a scavenger mixture for said tetramethyllead consisting essentially of a halohydrocarbon scavenger and aryl phosphate in an amount of 0.05 to 2 theories.

The improved leaded gasoline compositions of the invention show unexpectedly high octane numbers compared to previously known combinations of hydrocarbon base fuels and conventional tetraethyllead antiknock agent. Such an increase in octane number has a particular advantage in that less lead is required for a given octane number. The lead metal is thus conserved and the likelihood of lead pollutants in the engine exhaust is substantially reduced. The present compositions have another important advantage in that the tetramethyllead and aryl phosphate together give a distinct reduction in preignition in actual engine operation.

The hydrocarbon base fuels of the compositions according to the invention are prepared by conventional refining and blending processes. They normally contain straight-chain paraffins, branched-chain paraffins, olefins, aromatics and naphthenes.

As already mentioned, the base fuels are hydrocarbon fuels boiling in the gasoline boiling range. Generally described, such fuels have an ASTM (D-86) disillation with an initial boiling point of about 100° F. and a final boiling point of about 425° F. The unleaded base fuels have a Research octane number of at least 90 as determined by the accepted CFR engine test method. The base fuels contain at least 20% and preferably 30% by volume of aromatic hydrocarbons. Preferably less than 30% by volume of olefinic hydrocarbons are present in the fuels. The total paraffin and naphthene hydrocarbon content of the fuels may be as much as 80% by volume.

For practical purposes, amounts of not more than about 4 ml. of lead compounds per gallon are ordinarily used in the compositions. Preferably at least 0.5 ml. or, still better, at least 1 ml. of tetramethyllead is present. If desired, other octane improving additives may be employed in addition to the tetramethyllead. These include other lead compounds such as tetraethyllead, carbonyl derivatives of iron and cyclopentadienyl derivatives of metals such as manganese or iron.

The aryl phosphates are esters of phosphoric acid. They are conveniently prepared by the reaction of hydroxyaromatic compounds, for example, phenols or alkyl phenols and mixtures thereof, including aliphatic alcohols of from 1 to 12 carbon atoms. Such aryl phosphate esters contain from 1 to 3 aryl groups. The alkylphenyl esters are generally preferred. The alkylphenyl groups contain at least 1 alkyl substituent having up to about 12 carbon atoms.

Examples of aryl phosphates within the scope of the present invention are as follows:

m-cresyl diphenyl phosphate
methyl diphenyl phosphate
tri(m-cresyl) phosphate
methyl di(m-cresyl) phosphate
triphenyl phosphate
methyl di(nonylphenyl) phosphate
dodecylphenyl dimethyl phosphate
m-cresyl diamyl phosphate
tri(2,4-dimethyl phenyl) phosphate
diphenyl β-naphthyl phosphate

The scavenger mixture for the tetramethyllead in the compositions according to this invention is any of the halohydrocarbon scavengers in common use such as ethylene dichloride, ethylene dibromide and mixtures thereof, propylene hexachloride, dichloropropane and the like.

The aryl phosphate esters are present in the gasoline compositions generally in amounts of from about 0.05 to 2 theories as mentioned above. A theory means that for each 3 grams atoms of lead in the antiknock compound there are 2 gram atoms of phosphorus in the aryl phosphate ester. This expression of the ratio of the aryl phosphate and the lead antiknock agent is based on the reaction of phosphorus and lead which proceeds to give lead orthophosphate of the formula $Pb_3(PO_4)_2$. The halohydrocarbon scavenger is employed in a theory ratio of scavenger to aryl phosphate in the range of from about

is to say that 2.06 ml./gal. of tetramethyllead is compared with 3.00 ml./gal. tetraethyllead because of the difference in densities and molecular weights of the compounds. The "improvement" is the difference in the octane number obtained with tetramethyllead less the octane number obtained with the equivalent amount of tetraethyllead.

TABLE I

Ex. no.	Hydrocarbon composition: Paraffins and naphthenes, vol. percent	Hydrocarbon composition: Olefins, vol. percent	Hydrocarbon composition: Aromatics, vol. percent	Research octane unleaded	Motor octane: TML Ml.	Motor octane: TML No.	Motor octane: TEL Ml.	Motor octane: TEL No.	Improvement	Road octane: TML Ml.	Road octane: TML No.	Road octane: TEL Ml.	Road octane: TEL No.	Improvement	No. of cars
1	51	25	24	93.3	2.06	87.6	3.0	87.0	0.6	2.06	96.7	3.0	96.0	0.7	6
2	44	30	26	94.5	2.06	87.1	3.0	86.6	0.5	2.06	97.6	3.0	97.0	0.6	6
3	29	29	42	98.3	2.06	88.5	3.0	87.4	1.1	2.06	98.5	3.0	97.6	0.9	6
4	47	20	33	94.1	2.06	89.0	3.0	88.3	0.7	2.06	98.2	3.0	97.3	0.9	3
5	38	25	37	97.2	2.06	89.0	3.0	88.2	0.8	2.06	99.2	3.0	98.2	1.0	6
6	53	11	36	97.2	2.06	92.5	3.0	90.7	1.8	2.06	100.2	3.0	98.6	1.4	3
7	54	Trace	46	98.1	2.06	96.5	3.0	95.2	1.3	2.06	105.8	3.0	104.0	1.8	3
8	76	0	24	97.4	2.06	100.4	3.0	100.1	0.3	2.06	107.0	3.0	106.5	0.5	3
9	76	0	24	97.4	0.69	95.2	1.0	95.2	0.0	0.69	103.2	1.0	104.0	−0.8	1
10	44	30	26	94.5	0.69	84.8	1.0	84.2	0.6	0.69	97.4	1.0	98.9	−1.5	1
11	54	1	45	98.6	0.69	92.9	1.0	92.4	0.5	0.69	104.8	1.0	105.1	−0.3	1
12	41	16	43	95.6	0.69	86.2	1.0	85.2	1.0	0.69	95.1	1.0	95.2	−0.1	5
13	41	16	43	95.6	2.06	88.6	3.0	87.8	0.8	2.06	98.0	3.0	96.8	1.2	6
14	41	16	43	95.6	4.12	90.8	6.0	90.1	0.7	4.12	99.6	6.0	98.2	1.4	3
15	100	0	0	91.3	2.06	103.6	3.0	107.3	−3.7	2.06	102.6	3.0	104.0	−1.4	4
16	82	15	3	84.7	2.06	60.7	3.0	63.8	−3.1	2.06	92.7	3.0	93.4	−0.7	4
17	64	31	5	65.5	2.06	72.8	3.0	75.0	−2.2	2.06	80.9	3.0	83.1	−2.2	3
18	73	10	17	------	2.06	95.8	3.0	97.2	−1.4	------	------	------	------	------	------
19	30	40	30	78.4	2.06	84.2	3.0	84.9	−0.7	2.06	92.0	3.0	92.1	−0.1	4
20	37	1	62	99.8	2.06	90.4	3.0	88.8	1.6	2.06	105.1	3.0	101.9	+3.2	4
21	8	19	73	102.5	2.06	91.9	3.0	91.0	0.9	2.06	102.6	3.0	101.0	+1.6	4
22	0	0	100	108.7	2.06	102.8	3.0	101.3	1.5	2.06	111.7	3.0	107.6	+4.1	1
23	10	90	0	92.9	2.06	86.8	3.0	87.5	−0.7	2.06	95.6	3.0	96.1	−0.5	4
24	70	10	20	100.1	2.06	100.5	3.0	100.6	−0.1	2.06	106.8	3.0	105.5	+1.3	4
25	69	1	30	52.6	2.06	73.4	3.0	74.1	−0.7	Impossible to run in modern cars.					

0.5:1 to about 50:1 and preferably between about 1:1 and about 15:1.

The superior new leaded gasoline compositions of the invention are further illustrated by the following examples. These examples show typical test results on a number of compositions according to the invention in comparison with conventional high octane gasolines containing tetraethyllead.

The following tables are summaries of the pertinent data of the examples. The type of compositions of the hydrocarbon base fuel is shown with respect to the percent by volume of the paraffins and naphthenes, olefins and aromatics. The clear octane number of the base fuel is also given. This octane number, as already mentioned, is the accepted Research octane number which is usually employed in designating a given gasoline. This method is described as Research Method D–908 in "ASTM Manual of Engine Test Methods for Rating Fuels."

The first table, Table I, shows the effect on octane number by the addition of certain amounts of tetramethyllead, as compared to tetraethyllead. The octane number in this comparison is based on the Motor Method D–357 of the "ASTM Manual of Engine Test Methods for Rating Fuels." This method, which is more stringent than the Research Method, illustrates more accurately the desirable qualities of the improved gasoline compositions of the invention.

The effect of the improved gasoline compositions of the invention is also shown by the road octane ratings in the table. These ratings are determined by chassis dynamometer tests in accordance with the accepted Modified Uniontown Test Procedure. In these determinations, eight different makes of automobiles of recent manufacture (1956–1958) were employed, some of which were modified to provide increased compression ratios. At standard timing, the octane requirement of these automobiles ranges from about 94 to 102 octane numbers. The compression ratios vary from about 8.5 to 1 to as high as about 12 to 1.

In Table I, the rating of tetramethyllead (TML) compared with tetraethyllead (TEL) is based on gasoline compositions containing an equal lead concentration. That

The examples summarized in the above table show that the improved gasoline compositions of the invention containing tetramethyllead are decidedly better on the basis of octane number rating than comparable gasoline compositions of the type known heretofore. The hydrocarbon base fuels having a clear (unleaded) octane number of at least 90 in combination with about 1.0 ml. of tetramethyllead provide a gasoline composition of much greater road octane number improvement than can be obtained with similar hydrocarbon base fuels containing either tetraethyllead or less than 1.0 ml. of tetramethyllead. The compositions having at least 20% by volume of aromatic hydrocarbons are greatly superior to similar compositions lesser amounts of aromatic hydrocarbons.

The effectiveness of the improved leaded gasoline compositions of the invention is further illustrated by additional examples in Table II which follows. In these examples, test results are given showing that the gasolines of the invention have distinctly improved surface ignition characteristics.

The surface ignition tests are carried out in a single cylinder L-head CFR engine. Such test engines are of the type described by Hirschler et al. on pages 44 to 45, inclusive, of volume 62 of "SAE Transactions for 1954." The engine is run for 100 hours at full throttle at a steady rate of 900 r.p.m. The jacket temperature of the engine is maintained at about 150° F. and the crankcase temperature at about 140° F. The air:fuel ratio was roughly 13:1. The engine head is fitted with a single spark plug and a pressure sensitive magnetostrictive pickup which transmits rate of change of pressure pulses to a thyratron counting circuit. The number of surface ignition counts per hour is noted.

The base fuel was a typical high octane hydrocarbon composition boiling in the gasoline range containing 51% by volume paraffins and naphthenes, 25% olefins and 24% aromatics. It had a Research Method D–908 octane number of about 94. For the purposes of the tests the base fuel is leaded with 3 ml./gal. of tetraethyllead plus 1 theory of ethylene bromide scavenger for comparison with the equivalent of 2.06 ml./gal. of tetramethyllead plus scavenger. The amounts of lead are thus equal in each type of gasoline. The aryl phosphate ester was a typical ester as mentioned in the foregoing description, namely, tricresyl phosphate.

TABLE II

Gasoline:	Surface ignition counts per hour
Base gasoline containing TEL and 0.2 theories tricresyl phosphate	17
Base gasoline containing tetramethyllead and 0.2 theories tricresyl phosphate	8

The test data of the above Table II show that the improved leaded gasoline compositions according to the invention which contain tetramethyllead and aryl phosphate ester are remarkably superior from the standpoint of surface ignition compared to similar compositions containing conventional tetraethyllead antiknock agent. The tetramethyllead composition gives sharply reduced surface ignition counts of less than half those encountered with tetraethyllead.

The effectiveness of the combination of tetramethyllead and aryl phosphate ester in aromatic high octane gasolines is also shown in further tests giving Motor Method octane number ratings and road octane number ratings. In these tests, the gasoline base stock was the same as that used in the examples of Table II. The tetramethyllead and the conventional tetraethyllead were employed in amounts sufficient to give 3.17 g. of lead per gallon. This is equivalent to 3 ml. of tetraethyllead per gallon or 2.06 ml. of tetramethyllead. One theory of ethylene dibromide scavenger was also used. The phosphorus additive in these tests was cresyl diphenyl phosphate, another typical aryl phosphate ester. The road octane number was based on the 3-car averages of a 1958 Mercury, a 1957 Buick and a 1959 Ford.

TABLE III

Gasoline	Motor octane		Road octane
	TEL	TML	TML
Base gasoline containing 3.17 g. of lead per gal. without phosphorus additive	87.4	88.6	97.7
Base gasoline containing 3.17 g. of lead per gal. plus 0.5 theories cresyl diphenyl phosphate	87.3	88.8	97.9

The above test results show that the combination of

tetramethyllead and aryl phosphate ester additive is surprisingly free of antagonistic reactions between the two compounds and actually shows some improvement. The tetramethyllead compositions which already have a higher octane number than the corresponding tetraethyllead compositions are substantially improved by the addition of the aryl phosphate ester, whereas the tetraethyllead composition octane number is adversely affected by the addition of the phosphate ester.

What is claimed is:

1. A hydrocarbon base fuel boiling in the gasoline boiling range for spark ignition internal combustion engines having a clear Research octane number of at least 90 and containing at least 20% by volume of aromatic hydrocarbons said fuel containing from 1 to about 4 ml. of tetramethyllead, a scavenger mixture for said tetramethyllead consisting essentially of halohydrocarbon scavenger and aryl phosphate ester selected from the group consisting of cresyl diphenyl phosphate and tricresyl phosphate, in an amount of 0.05 to 2 theories, said halohydrocarbon scavenger being present in a theory ratio of scavenger to phosphate in the range of from about 0.5:1 to about 50:1, said fuel having a Motor Method octane number and an average Road octane number greater than the corresponding octane numbers of a mixture of said hydrocarbon composition containing a molar equivalent of tetraethyllead.

2. A hydrocarbon base fuel in accordance with claim **1** wherein the halohydrocarbon scavenger is ethylene dibromide and the aryl phosphate ester is tricresyl phosphate.

3. A hydrocarbon base fuel in accordance with claim **1**, wherein the halohydrocarbon scavenger is ethylenedibromide and the arylphosphate ester is cresyldiphenyl phosphate.

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