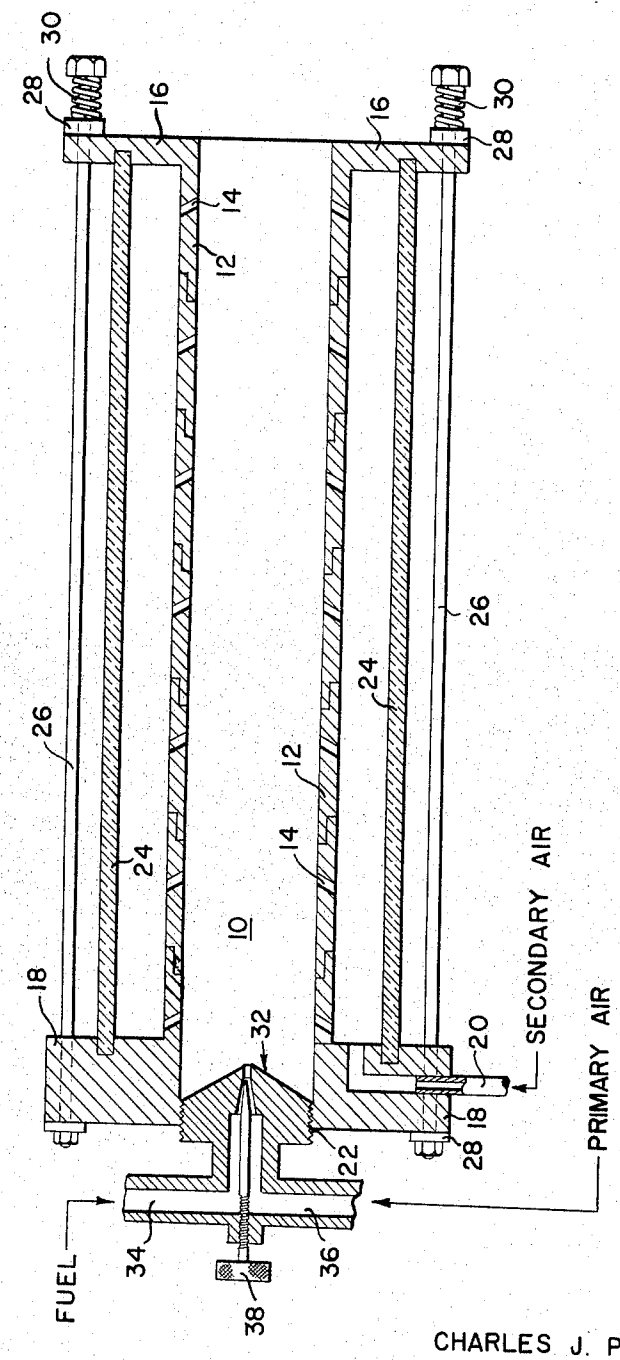
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LIQUID HYDROCARBON FUELS

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LIQUID HYDROCARBON FUELS

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This is a continuation-in-part of my copending application Ser. No. 277,553 filed Mar. 19, 1952, now abandoned.

This invention relates to normally liquid hydrocarbon fuels and more particularly to a novel addition agent for improving such fuels and to such fuels containing such agent.

Tetraethyl lead is commonly employed today as an antiknock agent for motor fuels for spark ignition engines. It is quite toxic and readily enters the body, both through the skin and through the lungs, and decomposes to deposit lead in the bloodstream. Through the use of proper precautions, the hazards in the manufacture and use of tetraethyl lead have been effectively controlled. Besides its use in the manufacture of tetraethyl lead, lead has many other valuable uses and there are times when the lead becomes scarce and the other valuable uses conflict with its use in tetraethyl lead. Accordingly, there has long been a continued interest in the discovery of other antiknock agents which can be made more cheaply from cheaper and more readily available materials and which, preferably, are less toxic.

The compound, which has been most widely considered as an antiknock agent to be substituted for tetraethyl lead, is iron pentacarbonyl which is easily made from readily available iron and carbon monoxide. Such iron pentacarbonyl is also very toxic and unstable, decomposing to release carbon monoxide, and enters the body readily both through the skin and through the lungs. It decomposes rapidly and sometimes ignites on exposure to the air. It also decomposes when exposed to light, even in dilute solution in gasoline, giving insoluble $Fe_2(CO)_9$ and toxic carbon monoxide. Accordingly, in addition to requiring careful precautions due to toxicity hazards, the iron pentacarbonyl, and gasoline containing it, must also be protected from air and light at all times. Some of such disadvantageous properties of iron pentacarbonyl and an attempt to solve them are disclosed by Lamping in patent No. 2,149,221.

Deposits of carbon are normally formed when liquid hydrocarbon fuel oils are burned in an excess of air in conventional burning devices. Even in simple furnaces, such deposits cause trouble by clogging burners and other parts and must usually be removed mechanically. In the more intricate devices for utilizing liquid fuel oils, such as diesel engines and gas turbine engines and, particularly, the jet turbines used in airplanes, the formation of such deposits is especially objectionable. The deposits change the flow pattern of the gases and hence reduce the efficiency of the engine. An even more serious effect is to cause warping of the various parts, in some cases further altering the flow pattern (for example by deformation of the combustion chamber liner), and in others making structures such as turbine blades ineffective, since their precise dimensions are critical.

Moreover, the incomplete combustion of liquid fuel oils also causes trouble through the presence of soot dispersed in the combustion gases. Thus, domestic oil burners and diese locomotives and trucks cause annoyance and damage in congested areas by contaminating the atmosphere with soot and forming smog. Similarly, carbon particles in the exhaust from jet engines are believed to be largely responsible for forming vapor tracks, and contribute directly to visibility, effects which are obviously highly undesirable in the case of military aircraft.

It is an object of the present invention to provide normally liquid hydrocarbon fuels containing a novel addition agent which improves the ignition and combustion characteristics of the fuels. Another object is to provide normally liquid hydrocarbon motor fuels for spark ignition engines containing a novel antiknock agent or mixture of antiknock agents. A further object is to provide a novel antiknock mixture. A still further object is to provide normally liquid hydrocarbon fuel oils containing a novel addition agent which improves the combustion characteristics of such fuel oils. Other objects are to provide new compositions of matter and to advance the art. Still other objects will appear hereinafter.

The above and other objects may be accomplished in accordance with this invention which comprises incorporating in a normally liquid hydrocarbon fuel from about 0.001% to about 1% by weight of organic compound containing the dicyclopentadienyliron nucleus which is soluble in the fuel and which is a member of the class consisting of dicyclopentadienyliron and substituted dicyclopentadienylirons in which the substituents are on the cyclopentadienyl rings and consist of 1 to 4 members of the class consisting of hydrocarbon radicals of 1 to 12 carbon atoms, monohalogenated hydrocarbon radicals of 1 to 12 carbon atoms in which the halogen atom has an atomic weight of at least 35, organic radicals consisting of 1 to 12 carbon atoms, 1 oxygen atom and the rest hydrogen atoms, amino groups, monoaminoalkyl radicals of 1 to 12 carbon atoms, and a second dicyclopentadienyliron nucleus joined to the first mentioned dicyclopentadienyliron nucleus by two divalent hydrocarbon bridging radicals each of which contains 1 to 12 carbon atoms, there bing no more than two of such substituents on any one cyclopentadienyl ring.

The normally liquid hydrocarbon fuels of this invention include motor fuels for spark ignition engines and fuel oils. The motor fuels for spark ignition engines consist essentially of normally liquid hydrocarbons in the gasoline boiling range, i.e., in the range of from about 100° F. to about 400° F. Such motor fuels will be composed preponderantly of aliphatic hydrocarbons, including cycloaliphatic hydrocarbons such as the naphthenes, and will have an A.P.I. gravity of at least 50, usually between 50 and 70. They include straight-run gasolines, cracked gasolines, synthetic gasolines, pure hydrocarbons such as n-heptane, methylcyclohexane, isooctane, and the like, and blends of two or more of such gasolines and hydrocarbons.

The fuel oils have an A.P.I. gravity below 50, usually from about 30 to about 46, and an end distillation point of at least 480° F. They include furnace oils, diesel fuels and kerosenes, including, particularly, the hydrocarbon fuels that are suitable for use in gas turbine engines and especially those used in jet engines employed in aircraft. They may be natural straight-run, cracked or synthetic products or blends of any two or more thereof.

Dicyclopentadienyliron and the substituted dicyclopentadienylirons of this invention have been found to materially improve the ignition and combustion characteristics of the fuels. When the fuel is a motor fuel for spark ignition engines, the compounds are effective to confer valuable antiknock properties thereto, particularly, when they are present in a proportion of from about 0.01% to about 1% by weight of the motor fuel. The motor fuels may also contain tetraethyl lead, and the compounds of this invention will further improve the knock rating of the motor fuel over that produced by the tetraethyl lead alone. The dicyclopentadienyliron and its substitution derivatives of this invention may be mixed with tetraethyl lead to produce new and valuable antiknock mixtures.

Dicyclopentadienyliron and the substituted dicyclopentadienylirons of this invention are of special value in fuel oils where they materially improve the combustion characteristics of such oils, greatly decreasing their tendency to form soot in the exhaust gases and solid carbonaceous deposits in the combustion apparatus, the deposits which are formed containing only small percentages of iron. They are far superior to other compounds proposed for this purpose and hence are particularly suitable for use in fuel oils employed in gas turbine engines, especially in jet engines, and wherever such fuel oils are burned in air.

Dicyclopentadienyliron was first disclosed by Kealy and Pauson and it and a suitable method of preparing it are disclosed in their article on pages 1039 and 1040 of Nature, vol. 168, No. 4285, published Dec. 15, 1951 by MacMillan & Co., Ltd. of London, and by Pauson in his copending application, Ser. No. 291,567 filed June 3, 1952 now U.S. Patent 2,650,756.

Dicyclopentadienyliron is a stable solid, melting at about 173° C. to 174° C. and subliming in air at temperatures as low as 100° C., without decomposition and is not spontaneously inflammable in air, which facts indicate considerable stability to oxidation. It is soluble in liquid hydrocarbons, and is the preferred compound of this invention. Its starting materials, iron or iron salts and cyclopentadiene, are readily available and relatively inexpensive. Its low volatility makes it much less hazardous to handle than iron pentacarbonyl. While its toxicity has not been fully investigated, its normal decomposition products are not carbon monoxide or lead and hence it should be very much less toxic than iron pentacarbonyl and tetraethyl lead. It dissolves very readily in benzene to form a yellow solution. No spontaneous inflammability was observed, even when a benzene solution was evaporated on filter paper. The substituted dicyclopentadienylirons of this invention have similar advantageous properties such as stability, relatively low volatility as compared to iron pentacarbonyl and normal decomposition products of relatively low toxicity, and are not spontaneously inflammable.

Woodward, Rosenblum and Whiting, in their article appearing on pages 3458 and 3459 of J.A.C.S., 74 of July 6, 1952 disclose that dicyclopentadienyliron has a rare sandwich structure, the atom of iron being sandwiched between two cyclopentadienyl rings in which all carbon atoms are equivalent.

The substituted dicyclopentadienylirons, which may be employed in accordance with this invention, are those which are soluble in the hydrocarbon fuels and which are members of the classes consisting of:

(1) Those in which the substituents consist of 1 to 4 hydrocarbon radicals of 1 to 12 carbon atoms such as bis(methyl cyclopentadienyl)iron, (ethyl cyclopentadienyl)cyclopentadienyliron, bis(diphenyl cyclopentadienyl)iron and bis(dicyclohexyl cyclopentadienyl)iron which may be prepared by the methods disclosed by Graham and Whitman in their copending application Ser. No. 352,294, filed Apr. 30, 1953, now abandoned; (cyclopentenyl cyclopentadienyl)cyclopentadienyliron, a yellow crystalline solid melting at 66–67° C. and which is prepared by dissolving dicyclopentadienyliron in liquid hydrogen fluoride at 100° C., precipitating the product by drowning the mixture in water and then purifying the product by distillation, and (cyclopentyl cyclopentadienyl) cyclopentadienyliron, a yellow oil, freezing at 15–16° C., boiling at 160–165° C. at 10 mm., giving a yellow color in sulfuric acid turning to green, and which is prepared by hydrogenating (cyclopentenyl cyclopentadienyl)cyclopentadienyliron with a mixed palladium and platinum catalyst at 50 pounds pressure and 25–35° C. in methanol solution; monophenyl bis(cyclopentadienyl)iron, bis (phenyl cyclopentadienyl)iron, tri(p-diphenyl)bis(cyclopentadienyl)iron and bis(p-diphenyl cyclopentadienyl) iron which may be prepared by the methods disclosed by Weinmayr in his copending application Ser. No. 352,283 filed Apr. 30, 1953, now abandoned;

(2) Those in which the substituents consist of a second dicyclopentadienyliron nucleus joined to the first such nucleus by two divalent hydrocarbon bridging radicals each of which contains 1 to 12 carbon atoms, such as methylene and phenylmethylene bridging radicals, which is the condensation product of 2 mols of dicyclopentadienyliron with 2 mols of an aldehyde with the elimination of 2 mols of water and which may be prepared by the methods disclosed by Weinmayr in his copending application Ser. No. 312,851 filed Oct. 2, 1952, now U.S. Patent 2,694,721;

(3) Those in which the substituents consist of monohalogenated hydrocarbon radicals of 1 to 12 carbon atoms in which the halogen atom has an atomic weight of at least 35 (chlorine, bromine and iodine), preferably chlorine, such as mono(p-chlorophenyl)bis(cyclopentadienyl) iron and bis(p-chlorophenyl cyclopentadienyl)iron which may be prepared by the methods disclosed by Weinmayr in his copending application Ser. No. 352,283 filed Apr. 30, 1953;

(4) Those in which the substituents are organic radicals consisting of 1 to 12 carbon atoms, 1 oxygen atom and the rest hydrogen atoms, such as the carboxaldehydes, represented by cyclopentadienyl(aldomethyl cyclopentadienyl)iron and bis(aldomethyl cyclopentadienyl)iron which may be prepared by the methods disclosed by Graham in his copending application Ser. No. 360,370 filed June 8, 1953, now U.S. Patent 2,849,469; the acyl derivatives represented by monoacetyl bis(cyclopentadienyl)iron which may be prepared by the method disclosed by Weinmayr in his copending application Ser. No. 352,029 filed Apr. 29, 1953, now U.S. Patent 2,988,562, and by diacetyl bis(cyclopentadienyl)iron which may be prepared by the method disclosed by Woodward et al. in J.A.C.S., 74, 3458 (1952); the hydroxyalkyl derivatives represented by cyclopentadienyl (hydroxymethyl cyclopentadienyl)iron and cyclopentadienyl (α-hydroxyethyl cyclopentadienyl)iron which may be made by the methods disclosed by Alfred C. Haven, Jr. in his copending application Ser. No. 365,558 filed July 1, 1953, now U.S. Patent 2,810,737; the hydroxyaryl derivatives represented by mono(p-hydroxyphenyl)bis(cyclopentadienyl) iron, which may be prepared by the methods disclosed by Weinmayr in his copending application Ser. No. 352,283 filed Apr. 30, 1953;

(5) Those in which the substituents are amino groups, represented by (amino cyclopentadienyl) cyclopentadienyliron, which may be prepared by the methods disclosed by Alfred C. Haven, Jr., in his copending application Ser. No. 365,556 filed July 1, 1953, now U.S. Patent 3,035,074;

(6) Those in which the substituents are monoaminoalkyl radicals of 1 to 12 carbon atoms, represented by (aminoethyl cyclopentadienyl) cyclopentadienyliron, which may be prepared by the methods disclosed by Graham and Whitman in their copending application Ser. No. 365,563 filed July 1, 1953, now U.S. Patent 2,859,233;

(7) Those in which there are 2 to 4 different substituents selected from the classes set forth in (1) to (6) inclusive, above; and

(8) Mixtures of two or more of dicyclopentadienyliron and such substituted dicyclopentadienylirons.

The amount of dicyclopentadienyliron or of substituted dicyclopentadienylirons, employed in a motor fuel for spark ignition engines, usually will vary from about 0.01% to about 1% by weight of the fuel and, preferably, from about 0.05% to about 0.3% by weight. When the motor fuel contains tetraethyl lead, the amount of the tetraethyl lead usually will be from about 0.03% to about 0.3% by weight and, preferably, from about 0.06% to about 0.3% by weight; 0.5 cc. of tetraethyl lead per gallon of motor fuel providing 0.03% by weight. Also, when the motor fuel contains tetraethyl lead, it will, in addition, ordinarily contain a lead scavenging agent in the amount of from

about 1 to about 5 theories, preferably from about 1 to about 2 theories, based on the tetraethyl lead. The lead scavening agents are well known to the art and are compounds which contain chlorine or bromine, the most commonly employed scavenging agents being ethylene dichloride and ethylene dibromide. One theory of a scavenging agent is that quantity which provides 2 atoms of active halogen per atom of lead.

A particularly valuable antiknock mixture for addition to a motor fuel for spark ignition engines will consist essentially of from about 0.01 to about 1 part by weight of dicyclopentadienyliron or an equivalent amount of a substituted dicyclopentadienyliron and from about 0.03 to about 0.3 part by weight of tetraethyl lead, preferably, from about 0.05 to about 0.3 part by weight of dicyclopentadienyliron and from about 0.06 to about 0.3 part by weight of tetraethyl lead. Also, preferably, such mixture will contain a lead scavenging agent in the amount of from about 1 to about 5 theories, based on the tetraethyl lead. Such mixture, most desirably, also contains a blending agent, such as an organic solvent which is a solvent for both the dicyclopentadienyliron and the tetraethyl lead. Suitable blending agents are liquid hydrocarbons, such as gasoline, kerosene, petroleum ether, benzene and isooctane. The preferred blending agent is benzene, the dicyclopentadienyliron being soluble therein in the amount of about 20% at room temperatures. The blending agent will be present in the mixture in an amount slightly in excess of that required to dissolve the dicyclopentadienyliron, and will usually constitute from about 25% to about 75% of the total weight of the mixture.

The amount of dicyclopentadienyliron or of a substituted dicyclopentadienyliron, employed in a normally liquid hydrocarbon fuel oil, usually will vary from about 0.001% to about 1% by weight of the fuel oil, preferably from about 0.005% to about 0.1% by weight. However, the amount will also depend, to a large extent, upon the use of the fuel oil, its normal tendency to form carbon, and the extent to which it is desired to eliminate carbon formation.

In order to test the performance of the fuel oils of the present invention rapidly in the laboratory, they were burned in a combustion apparatus which was designed to closely reproduce the conditions present in the combustion chamber of a gas turbine engine and to be readily disassembled for the removal, weighing, and analysis of the carbon deposits formed therein. The main essential features of such apparatus are shown in the accompanying drawing in which the single figure is a cross-sectional view, diagrammatical in character, of the combustion chamber assembly.

The combustion chamber **10** is made up of a number of interlocking rings **12** of stainless steel, 1 inch in internal diameter, 1 inch long and ⅛ inch thick, each provided with 4 equally spaced holes **14** having a diameter of ⅛ inch drilled at 60° to the center line. The ring, at the exhaust end of the chamber, is provided with a flange **16**. The ring, at the burner end of the chamber, is provided with a thick flange **18** having an inlet **20** for the admission of secondary air to the space surrounding the rings, and threaded internally at **22**. The combustion chamber is surrounded by a Pyrex tube **24** two inches in diameter having its ends fitting in notches in the opposing faces of the flanges **16** and **18** and forming a jacket spaced from the outer walls of the rings. The assemblage is held yieldingly together by three tie rods **26** provided with protective rings **28** and springs **30** to allow for the difference in thermal expansion of the combustion chamber rings **12** and the Pyrex tube **24** and to permit the rings **12** to be disassembled and taken out for ready removal of the deposits formed on their inner surfaces. A fuel-air nozzle **32** is screw fitted into the burner end of the chamber and is provided with a fuel oil inlet tube **34**, a primary air inlet tube **36** and a needle valve **38**.

In operation, the fuel oil was injected into the combustion chamber **10** by gravity, the flow rate being controlled by a calibrated rotameter (not shown) and by the needle valve **38**. The primary air, roughly about 10% of the total air, was introduced with the fuel oil through the nozzle **32** from inlet **36**, the volume being controlled by a calibrated flowmeter (not shown). The secondary air (roughly about 90% of the total air) was introduced through the inlet **20**, entered the space between the rings **12** and the Pyrex tube **24** and then passed through holes **14** into the combustion chamber **10**, the rate of supply being controlled by a calibrated flowmeter (not shown). The fuel-air mixture, flowing through the combustion chamber, was initially ignited by inserting a lighted Bunsen burner into the burner section. Immediately thereafter, the Bunsen burner was removed and the mixture continued to burn without the application of any external source of ignition.

Example I

Dicyclopentadienyliron or a substituted dicyclopentadienyliron was dissolved, in the amounts shown in the following tables, in a gasoline with an octane number of 60, composed entirely of paraffinic hydrocarbons. The octane numbers of these treated fuels were then determined, using the ASTM method D–908–48T, except that the fuel was directly injected into the engine cylinder instead of being passed through a carburetor. Comparative data for iron pentacarbonyl, in proportions containing the same amounts of iron per gallon, are included in the tables.

The engine, used for determining octane numbers by this method, is known as an ASTM–CFR (CFR=Co-operative Fuel Research) knock-rating engine, and the procedure as Research Rating Method (F–1). This Research Method has proved to give good correlation with operation of engines in automobiles on the road using present-day fuels, i.e., correlates with "road-rating" procedures.

The CFR test engine is a single-cylinder, four-stroke-cycle, valve-in-head engine of the variable-compression type, whereby the cylinder may be raised or lowered to vary the compression ratio from 3:1 to more than 10:1. Under the Research Method, the CFR engine is operated at 600 r.p.m. with the inlet air temperature maintained at 125° F., and the coolant at 212° F. In operation, the compression ratio is increased for a given fuel until knocking starts. The engine is calibrated by means of various reference fuels of known octane rating.

Table I compares the antiknock action of dicyclopentadienyliron and substituted dicyclopentadienylirons with that of iron pentacarbonyl.

TABLE I

Additive	Milli-atoms Fe per gal.	Grams per gal.	Wt. percent on fuel	Octane No.
Dicyclopentadienyliron	7.43	1.384	0.053	68.3
	14.86	2.768	0.106	71.0
	26.87	5.00	0.192	75.2
	44.6	8.31	0.319	79.5
Iron pentacarbonyl	7.43	1.457	0.056	64.4
	14.86	2.914	0.112	69.1
	26.87	5.26	0.202	76.2
	44.6	8.73	0.335	82.7
A. Bis (methyl cyclopentadienyl) iron.	7.43	1.59	0.061	69.1
B. (Cyclopentenyl cyclopentadienyl) cyclopentadienyliron, containing 17.8% iron.	14.86	3.18	0.122	71.8
	7.43	2.34	0.090	65.7
	14.86	4.68	0.180	68.0
D. Dicyclopentadienyliron having a second dicyclopentadienyliron nucleus joined thereto by two methylene bridging radicals	7.9	2.0	0.077	68.5
E. Monoacetyl dicyclopentadienyliron	7.4	2.0	0.077	65.1
F. Diacetyl dicyclopentadienyliron	10.6	2.1	0.081	66.7
G. (Cyclopentyl cyclopentadienyl) cyclopentadienyl iron.	7.4	1.88	0.072	67.3
	14.8	3.76	0.144	70.8

It will be seen from the above that the dicyclopentadienyliron and the substituted dicyclopentadienylirons generally are at least as effective as iron pentacarbonyl in equivalent iron concentrations, and also on a weight basis, over a wide range, and are more effective at the smaller concentrations. The effect, given by the lowest amount of dicyclopentadienyliron (1.384 g., containing 7.43 milliatoms of iron) in the table, would be produced by 0.725 cc. (1.2 g.) of tetraethyl lead per gallon, containing 3.73 milliatoms of lead.

Table II (below) compares the effects of dicyclopentadienyliron and substituted dicyclopentadienylirons with iron pentacarbonyl, when used with tetraethyl lead (TEL). It is known (see U.S. 2,398,282 of Bartholomew) that mixtures of tetraethyl lead and iron pentacarbonyl in some proportions are less effective or no more effective than the tetraethyl lead content used alone. Such a situation is shown below. When, however, the iron pentacarbonyl is replaced by an equivalent amount of dicyclopentadienyliron or of a substituted dicyclopentadienyliron very significant increases in antiknock effect are observed.

TABLE II

Additive	TEL cc. per gal.	Other Additive		Octane No.
		Wt. percent on fuel	Milliatoms Fe per gal.	
TEL	3.0			85.0
	1.0			71.7
TEL+iron pentacarbonyl	3.0	0.112	14.86	85.0
	1.0	0.112	14.86	75.7
TEL+dicyclopentadienyliron	3.0	0.106	14.86	89.7
	1.0	0.106	14.86	79.5
TEL+A (see Table I)	3.0	0.122	14.86	88.6
TEL+B (see Table I)	3.0	0.180	14.86	87.6
TEL+G (see Table I)	3.0	0.144	14.86	88.5

The dicyclopentadienyliron has also been shown to have valuable antiknock properties in simple pure hydrocarbons, such as n-heptane, methylcyclohexane, and 2-methylpentane.

The knock rating, obtained by the use of dicyclopentadienyliron, is deleteriously affected by sulfur compounds, such as diisoamyl disulfide, in the motor fuel, but to a considerably less degree than is tetraethyl lead.

Example II

The fuel oil employed was made up by adding 10% by volume of alpha-methylnaphthalene (to increase the tendency of the oil toward carbon formation) to a hydrocarbon fuel (a kerosene) of the following characteristics:

Gravity A.P.I.	45.7
Mercaptan sulfur, percent	0.002
Total sulfur, percent	0.270
Accelerated gum, mg./100 ml.	13.1
Existent gum (residue), mg./100 ml.	4.0
Total aromatics, vol. percent	21.6
Reid vapor pressure, #/sq. in.	2.9
Bromine number	7.2
Freezing point, ° F. (below)	−76
Aniline point, ° F.	113.7
Aniline-gravity constant	5196
Heat of combustion, net B.t.u./lb. (Calc.)	18504
Initial boiling point, ° F.	136
Percent evaporated:	
5	194
10	239
15	264
50	344
90	452
At 400° F.	75.0
Final boiling point, ° F.	518
Recovery, percent	98.0
Loss, percent	1.0
Residue, percent	1.0

To samples of such mixture were added dicyclopentadienyliron or other additive shown in Table III. Each 0.1 gram of additive per 100 ml. of fuel is equal to 0.125% by weight of additive based on the fuel. Such samples, together with untreated (control) samples of the mixture, were tested in the apparatus shown in the drawings by feeding the fuel through the nozzle at the rate of 150 ml. per hour with a primary air flow (also through the nozzle) of 100 cu. ft. per hour and a secondary air flow of 940 cu. ft. per hour, and burning the fuel-air mixture. After 250 ml. of each sample of fuel oil mixture had been burned in such apparatus, the rings were taken out of the apparatus and the deposits, formed on their inner surfaces, were carefully removed therefrom, weighed and, in some cases, analyzed. The results are shown in the following Table III in which the weights of the deposits are given in milligrams and the percent of carbon and of ash in representative deposits is also given.

TABLE III

Additive	Grams/100 ml. of fuel	Deposit, mg.	Carbon, percent	Ash, percent
Control	0	203		
Dicyclopentadienyliron	0.5	33		
Do	0.1	26	44	48
Control	0	286	80	0.23
Dicyclopentadienyliron	0.01	6	67	3.5
Control	0	220		
Dicyclopentadienyliron	0.01	10		
Do	0.005	11		2.0
Control	0	230		
Dicyclopentadienyliron	0.001	82		
Do	0.001	40		
Control	0	190		
Dicyclopentadienyliron	0.0005	149		
Iron pentacarbonyl [1]	0.105	59		
Iron pentacarbonyl [2]	0.0105	70		
Control	0	165		
Iron naphthenate [1]	0.54	164		
Iron naphthenate [2]	0.054	159		
Control	0	314		
(Phenyl cyclopentadienyl) cyclopentadienyliron [1]	0.14	28		
(Acetyl cyclopentadienyl) cyclopentadienyliron [2]	0.012	5		
(Amino cyclopentadienyl) cyclopentadienyliron [2]	0.0108	9		

[1] The amount employed in each case is equivalent to 0.1 gram of dicyclopentadienyliron.
[2] The amount employed in each case is equivalent to 0.01 gram of dicyclopentadienyliron.

In each case, where the fuel oil composition contained 0.00125% by weight or more of dicyclopentadienyliron or the iron pentacarbonyl, no visible carbon was observed in the exhaust gases whereas, in all other cases, the exhaust gases contained material amounts of visible carbon.

Example III

A fuel, composed of 25% by weight of kerosene and 75% by weight of No. 2 fuel oil, was subjected to the ASTM lamp test D–187–49 employing an ASTM No. 27 burner equipped with a Macbeth-Evans No. 514 pearl top chimney, with the wick adjusted to give a smoky flame such that the internal surfaces of the chimney were covered with a dense layer of soot at the end of ½ hour of operation. When such test was repeated with the same fuel to which had been added 0.2% by weight of dicyclopentadienyliron, the flame was not smoky and did not deposit any soot on the chimney but deposited only a slight yellow stain thereon, apparently resulting from the decomposition of dicyclopentadienyliron.

The above results clearly show that very small amounts of dicyclopentadienyliron are effective to greatly decrease the amount of carbon formed by the combustion of fuel oil compositions containing it, eliminating the presence of carbon (or soot) in the combustion gases and very materially decreasing the amount of deposits in the combustion apparatus. Similar results will be obtained in other types of combustion apparatus. When 0.02% by weight of dicyclopentadienyliron was incorporated in a conventional jet fuel (JP–4) and such fuel was burned in a

conventional jet engine, very significantly higher ratios of fuel to air were required to cause carbon to appear in the exhaust gases than when the same fuel, without the dicyclopentadienyliron, was burned similarly.

It will be understood that the preceding examples have been given for illustrative purposes solely and that this invention is not limited to the specific embodiments disclosed therein. The substituted dicyclopentadienylirons, the proportions of dicyclopentadienyliron and of the substituted dicyclopentadienylirons, the composition of the hydrocarbon fuels, and the like may be varied widely within the limits hereinbefore set forth in the general description without departing from the spirit or scope of this invention. The hydrocarbon fuels may also contain antioxidants, stabilizers, dyes, and other compounds which are commonly added to hydrocarbon fuels of such types.

It will be apparent that, by this invention, there are provided hydrocarbon fuels containing novel additive compounds which materially improve the ignition and combustion characteristics of the hydrocarbon fuels and which are far superior to related agents previously proposed for such purposes. In the case of motor fuels for spark ignition engines, the additives are at least equal to iron pentacarbonyl in antiknock effect, do not have the disadvantages of iron pentacarbonyl and have the advantage that they can be used with tetraethyl lead over a wide range of proportions to consistently improve the octane members of the motor fuels. Also, there are provided antiknock mixtures of dicyclopentadienyliron and substituted derivatives thereof with tetraethyl lead which are particularly valuable for addition to motor fuels for spark ignition engines and which improve the antiknock characteristics of such motor fuels. Furthermore, in the case of hydrocarbon fuel oils, there are provided additives which are extremely effective to improve the combustion of the fuel oils whereby the amount of carbon produced by their combustion is very greatly decreased so that little or no carbon or soot appears in the exhaust gases of the equipment in which they are burned and the amounts of the deposits formed in such equipment are greatly decreased. Accordingly, it is apparent that this invention constitutes a valuable advance in and contribution to the art.

What is claimed is:

1. A normally liquid hydrocarbon fuel consisting of hydrocarbons in the gasoline boiling range composed preponderantly of aliphatic hydrocarbons containing from about 0.001% to about 1% by weight of an organic compound containing the dicyclopentadienyliron nucleus which is soluble in the fuel and which is a member of the class consisting of dicyclopentadienyliron and substituted dicyclopentadienylirons in which the substituents are on the cyclopentadienyl rings and consist of 1 to 4 members of the class consisting of monohalogenated hydrocarbon radicals of 1 to 12 carbon atoms in which the halogen atom has an atomic weight of at least 35, oxygen-containing organic radicals consisting of 1 to 12 carbon atoms, 1 oxygen atom and the rest hydrogen atoms, amino groups, monoaminoalkyl radicals of 1 to 12 carbon atoms, and a second dicyclopentadienyliron nucleus joined to the first mentioned dicyclopentadienyliron nucleus by two divalent hydrocarbon bridging radicals each of which contains 1 to 12 carbon atoms, there being no more than two of such substituents on any one cyclopentadienyl ring.

2. A normally liquid hydrocarbon fuel consisting of hydrocarbons in the gasoline boiling range composed preponderantly of aliphatic hydrocarbons containing from about 0.001% to about 1% by weight of dicyclopentadienyliron.

3. A normally liquid hydrocarbon fuel of the group consisting of normally liquid hydrocarbons in the gasoline boiling range composed preponderantly of aliphatic hydrocrabons and of fuel oils having an A.P.I. gravity of from about 30 to about 46 and an end distillation point of at least 480° F., said fuel containing from about 0.001% to about 1% by weight of an organic compound which consists of two dicyclopentadienyliron nuclei joined together by two divalent hydrocarbon bridging radicals each of which contains 1 to 12 carbon atoms.

4. A normally liquid hydrocarbon fuel of the group consisting of normally liquid hydrocarbons in the gasoline boiling range composed preponderantly of aliphatic hydrocarbons and of fuel oils having an A.P.I. gravity of from about 30 to about 46 and an end distillation point of at least 480° F., said fuel containing from about 0.001% to about 1% by weight of the organic compound which consists of two dicyclopentadienyliron nuclei joined together by two methylene bridging radicals.

5. A normally liquid hydrocarbon fuel of the group consisting of normally liquid hydrocarbons in the gasoline boiling range composed preponderantly of aliphatic hydrocarbons and of fuel oils having an A.P.I. gravity of from about 30 to about 46 and an end distillation point of at least 480° F., said fuel containing from about 0.001% to about 1% by weight of an organic compound which is soluble in the fuel and which is a substituted dicyclopentadienyliron in which the substituents consist of 1 to 4 monohalogenated hydrocarbon radicals of 1 to 12 carbon atoms in which the halogen atom has an atomic weight of at least 35, each substituent being on one of the cyclopentadienyl rings and there being not more than 2 substituents on any one cyclopentadienyl ring.

6. A normally liquid hydrocarbon fuel of the group consisting of normally liquid hydrocarbons in the gasoline boiling range composed preponderantly of aliphatic hydrocarbons and of fuel oils having an A.P.I. gravity of from about 30 to about 46 and an end distillation point of at least 480° F., said fuel containing from about 0.001% to about 1% by weight of an organic compound which is soluble in the fuel and which is a substituted dicyclopentadienyliron in which the substituents consist of 1 to 4 oxygen-containing organic radicals consisting of 1 to 12 carbon atoms, 1 oxygen atom and the rest hydrogen atoms, each substituent being on one of the cyclopentadienyl rings and there being not more than 2 substituents on any one cyclopentadienyl ring.

7. A motor fuel for spark ignition engines which consists essentially of normally liquid hydrocarbons in the gasoline boiling range and is composed preponderantly of aliphatic hydrocarbons and from about 0.01% to about 1% by weight of an organic compound containing the dicyclopentadienyliron nucleus which is soluble in the motor fuel and which is a member of the class consisting of dicyclopentadienyliron and substituted dicyclopentadienylirons in which the substituents are on the cyclopentadienyl rings and consist of 1 to 4 members of the class consisting of monohalogenated hydrocarbon radicals of 1 to 12 carbon atoms in which the halogen atom has an atomic weight of at least 35, oxygen-containing organic radicals consisting of 1 to 12 carbon atoms, 1 oxygen atom and the rest hydrogen atoms, amino groups, monoaminoalkyl radicals of 1 to 12 carbon atoms, and a second dicyclopentadienyliron nucleus joined to the first mentioned dicyclopentadienyliron nucleus by two divalent hydrocarbon bridging radicals each of which contains 1 to 12 carbon atoms, there being no more than two of such substituents on any one cyclopentadienyl ring.

8. A motor fuel for spark ignition engines which consists essentially of normally liquid hydrocarbons in the gasoline boiling range and is composed preponderantly of aliphatic hydrocarbons and from about 0.01% to about 1% by weight of dicyclopentadienyliron.

9. A motor fuel for spark ignition engines which consists essentially of normally liquid hydrocarbons in the gasoline boiling range and is composed preponderantly of aliphatic hydrocarbons, from about 0.01% to about 1% by weight of dicyclopentadienyliron and from about 0.03% to about 0.3% by weight of tetraethyl lead.

10. A motor fuel for spark ignition engines which consists essentially of normally liquid hydrocarbons in the gasoline boiling range and is composed preponderantly of aliphatic hydrocarbons and from about 0.01% to about 1% by weight of an organic compound which is soluble in the motor fuel and which consists of two dicyclopentadienyliron nuclei joined together by two divalent hydrocarbon bridging radicals each of which contains 1 to 12 carbon atoms.

11. An antiknock mixture consisting essentially of from about 0.03 to about 0.3 part by weight of tetraethyl lead and from about 0.01 to about 1 part by weight of an organic compound containing the dicyclopentadienyliron nucleus which is soluble in normally liquid hydrocarbons in the gasoline boiling range and which is a member of the class consisting of dicyclopentadienyliron and substituted dicyclopentadienylirons in which the substituents are on the cyclopentadienyl rings and consist of 1 to 4 members of the class consisting of hydrocarbon radicals of 1 to 12 carbon atoms, monohalogenated hydrocarbon radicals of 1 to 12 carbon atoms in which the halogen atom has an atomic weight of at least 35, oxygen containing organic radicals consisting of 1 to 12 carbon atoms, 1 oxygen atom and the rest hydrogen atoms, amino groups, monoaminoalkyl radicals of 1 to 12 carbon atoms, and a second dicyclopentadienyliron nucleus joined to the first mentioned dicyclopentadienyliron nucleus by two divalent hydrocarbon bridging radicals each of which contains 1 to 12 carbon atoms, there being no more than two of such substituents on any one cyclopentadienyl ring.

12. An antiknock mixture consisting essentially of from about 0.01 to about 1 part by weight of dicyclopentadienyliron and from about 0.03 to about 0.3 part by weight of tetraethyl lead.

13. A normally liquid hydrocarbon fuel oil having an A.P.I. gravity of from about 30 to about 46 and an end distillation point of at least 480° F. containing from about 0.001% to about 1% by weight of an organic compound containing the dicyclopentadienyliron nucleus which is soluble in the fuel oil and which is a member of the class consisting of substituted dicyclopentadienylirons in which the substituents are on the cyclopentadienyl rings and consist of 1 to 4 members of the class consisting of monohalogenated hydrocarbon radicals of 1 to 12 carbon atoms in which the halogen atom has an atomic weight of at least 35, oxygen-containing organic radicals consisting of 1 to 12 carbon atoms 1 oxygen atom and the rest hydrogen atoms, amino groups, monoaminoalkyl radicals of 1 to 12 carbon atoms, and a second dicyclopentadienyliron nucleus joined to the first mentioned dicyclopentadienyliron nucleus by two divalent hydrocarbon bridging radicals each of which contains 1 to 12 carbon atoms, there being no more than two of such substituents on any one cyclopentadienyl ring.

14. A normally liquid hydrocarbon fuel oil having an A.P.I. gravity of from about 30 to about 46 and an end distillation point of at least 480° F. containing from about 0.001% to about 1% by weight of an organic compound which is soluble in the fuel oil and which consists of two dicyclopentadienyliron nuclei joined together by two divalent hydrocarbon bridging radicals each of which contains 1 to 12 carbon atoms.

15. Gasoline containing from about 0.01% to about 1% by weight of a gasoline-soluble organic compound containing the dicyclopentadienyliron nucleus and which is a member of the class consisting of dicyclopentadienyliron and substituted dicyclopentadienylirons in which the substituents are on the cyclopentadienyl rings and consist of 1 to 4 members of the class consisting of monohalogenated hydrocarbon radicals of 1 to 12 carbon atoms in which the halogen atom has an atomic weight of at least 35, oxygen-containing organic radicals consisting of 1 to 12 carbon atoms, 1 oxygen atom and the rest hydrogen atoms, amino groups, monoaminoalkyl radicals of 1 to 12 carbon atoms, and a second dicyclopentadienyliron nucleus joined to the first mentioned dicyclopentadienyliron nucleus by two divalent hydrocarbon bridging radicals each of which contains 1 to 12 carbon atoms, there being no more than two of such substituents on any one cyclopentadienyl ring.

16. Gasoline containing from about 0.01% to about 1% by weight of dicyclopentadienyliron.

17. A fuel for internal combustion engines comprising hydrocarbons of the gasoline boiling range and an amount of dicyclopentadienyliron sufficient to raise the anti-knock characteristics of said fuel.

18. A liquid hydrocarbon fuel containing dicyclopentadienyliron in an amount sufficient to increase the anti-knock characteristics of said fuel.

19. A fuel for internal combustion engines consisting essentially of normally liquid hydrocarbons in the gasoline boiling range composed preponderantly of aliphatic hydrocarbons and a small proportion, sufficient to increase the anti-knock characteristics of said fuel, of dicyclopentadienyliron.

20. A method of operating an internal combustion engine which includes the step of supplying to the engine for combustion therein a fuel which consists essentially of normally liquid hydrocarbons in the gasoline boiling range and a small proportion, sufficient to increase the anti-knock characteristics of said fuel, of dicyclopentadienyliron.

21. A method of operating a spark ignition internal combustion engine which includes the step of supplying to the engine for combustion therein a fuel which consists essentially of normally liquid hydrocarbons in the gasoline boiling range and from about 0.001% to about 1% by weight of dicyclopentadienyliron.

22. Gasoline fuel for spark-ignition internal combustion engines containing tetraethyllead and a minor amount, sufficient to further enhance the antiknock response thereof, of bis-(alkylcyclopentadienyl) iron.

23. Gasoline fuel for spark-ignition internal combustion engines, containing an alkyllead and a minor amount, sufficient to further enhance the antiknock response thereof, of a lower-alkyl-substituted bis(cyclopetadienyl) iron.

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