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ANTIKNOCK COMPOUNDS FOR GASOLINE FUELS

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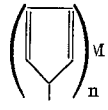
This invention relates to novel fuel compositions. In particular, our invention relates to fuels of improved antiknock quality containing compounds of metallic cyclopentadienyl-type.

Attendant with the development and evolution of the internal combustion engine for passenger car and heavy duty service, the petroleum industry has been continually called upon to effect improvements in the antiknock qualities of hydrocarbon fuels. These improvements have, in general, been brought about by two distinct methods. One of these methods comprises improvements in refining operations, such as thermal and catalytic cracking, and reforming or alkylating processes. The other method comprises the use of fuel additives to effect an increase in the antiknock qualities of the hydrocarbon fuels. Inasmuch as improvements in refinery techniques involve considerable capital expenditures, the use of fuel additives has attained greater and more widespread acceptance as the more effective method, particularly from the economic standpoint. The instant invention is therefore concerned with the improvement of hydrocarbon fuels with respect to ignition qualities and combustion characteristics. Other important considerations in addition to the antiknock effectiveness of antiknock materials include hydrocarbon solubility, stability, toxicity, and the like.

It is, therefore, an object of our invention to provide novel fuel compositions of improved ignition qualities and combustion characteristics. An additional object of our invention is to provide a general class of effective and stable antiknock additives for hydrocarbon fuels. Additional important objects of our invention will become apparent from the discussion which hereinafter follows.

In accordance with the instant invention, we have provided fuel compositions containing a class of compounds wherein at least one cyclopentadienyl-containing radical is directly bonded to a metal atom through the methylene group; that is, a metallic cyclopentadienyl.

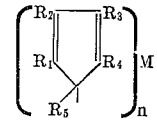
Thus, in one embodiment the fundamental structure of the antiknock agents of our invention can be represented by the general formula



wherein n is a small whole integer from one to four, and wherein M is a metallic element. Among the elements we can employ are copper, silver, and gold; that is, Group I–B of the Periodic Table. Likewise, we can employ beryllium, magnesium, calcium, strontium, barium, and radium; that is, Group II–A of the Periodic Table. Furthermore, we can employ zinc, cadmium, and mercury; that is, Group II–B of the Periodic Table. In addition, we can employ the elements of Group III–A of the Periodic Table; that is, boron, aluminum, gallium, indium, and thallium. Likewise, we can employ the elements of Group III–B of the Periodic Table; that is, scandium, yttrium, lanthanum, and actinium, including the lanthanum and actinium rare earth series of elements. Furthermore, we can employ the elements of Group IV–A of the Periodic Table; that is, silicon, germanium, tin, and

lead. In addition, we can employ the elements of Group IV–B of the Periodic Table; that is, titanium, zirconium, and hafnium. Likewise, we can employ the elements of Group V–A of the Periodic Table, such as arsenic, antimony, and bismuth. Furthermore, we can employ the elements of Group V–B of the Periodic Table; that is, vanadium, niobium, and tantalum. In addition, we can employ the elements of Group VI–A of the Periodic Table, such as selenium, tellurium, and polonium. Likewise, we can employ the elements of Group VI–B of the Periodic Table; that is, chromium, molybdenum, and tungsten. Furthermore, we can employ the elements of Group VII–B of the Periodic Table; that is, manganese, technetium, and rhenium. In addition, we can employ the elements of Group VIII of the Periodic Table; that is, iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, and platinum.

It is not intended that the scope of our invention be limited to the foregoing general formula which represents the basic or fundamental structure of the class of antiknock compounds of our invention, as the cyclopentadienyl moiety can be mono-, di-, tri-, tetra-, or penta-substituted with monovalent radicals, and in addition, said moiety can be directly bonded with at least one fused ring structure. For example, the cyclopentadienyl moiety can be substituted with monovalent radicals providing antiknock agents of the instant invention which can be represented by the general formula



wherein each of R_1, R_2, R_3, R_4, and R_5 can be the same or different and are selected from the class consisting of hydrogen and organic radicals; and wherein n and M are as described heretofore.

Thus, the R_1, R_2, R_3, R_4, and R_5 groups of the antiknock agents of our invention can be alkyl radicals such as, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, t-butyl, n-amyl, and the various positional isomers thereof as, for example, 1-methylbutyl, 2-methyl-butyl, 3-methyl-butyl, 1,1-dimethyl-propyl, 1,2-dimethyl-propyl, 2,2-dimethyl-propyl, and 1-ethyl-propyl, and likewise the corresponding straight and branched chain isomers, of hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octodecyl, nondecyl, eicosyl and the like. In addition, these monovalent hydrocarbon radicals may be alkenyl radicals such as ethenyl, Δ^1-propenyl, Δ^2-propenyl, isopropenyl, Δ^1-butenyl, Δ^2-butenyl, Δ^3-butenyl, and the corresponding branched chain isomers thereof as, for example, Δ^1-isobutenyl, Δ^2-isobutenyl, Δ^1-sec-butenyl, Δ^2-sec-butenyl, including 1-methylene-Δ^2-propenyl, Δ^1-pentenyl, Δ^2-pentenyl, Δ^3-pentenyl, Δ^4-pentenyl, and the corresponding branched chain isomers thereof; Δ^1-hexenyl, Δ^2-hexenyl, Δ^3-hexenyl, Δ^4-hexenyl, Δ^5-hexenyl, and the corresponding branched chain isomers thereof, including 3,3-dimethyl-Δ^1-butenyl; 2,3-dimethyl-Δ^1-butenyl; 2,3-dimethyl-Δ^2-butenyl; 2,3-dimethyl-Δ^3-butenyl; and 1-methyl-1-ethyl-Δ^2-propenyl; and similarly, the various isomers of heptenyl, octenyl, nonyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, eicosenyl, and the like.

Illustrative examples of alkyl substituted cyclopentadienyl metal compounds comprising the antiknock ingredients of our invention include, for example, such compounds as cyclopentadienyl boron, 2-methyl-cyclopentadienyl boron, 3-ethyl-cyclopentadienyl boron, 4-n-propyl-cyclopentadienyl boron, 5-isopropyl-cyclopentadienyl boron, 2,3-di-n-butyl-cyclopentadienyl boron, 2,4-

di-sec-butyl-cyclopentadienyl boron, 2,5-di-tert-butyl-cyclopentadienyl boron, cyclopentadienyl thallium, 2-n-amyl-cyclopentadienyl thallium, 3,4-di-(1-methyl-butyl)-cyclopentadienyl thallium, 2,3,4-trimethyl-cyclopentadienyl thallium, 2.3,4,5-tetraethyl-cyclopentadienyl thallium, cyclopentadienyl gallium, 3,4-di-n-octyl-cyclopentadienyl gallium, 2-ethenyl-cyclopentadienyl gallium, 3-(Δ^1-propenyl)-cyclopentadienyl gallium, 3,4-di-isopropenyl-cyclopentadienyl gallium, cyclopentadienyl indiuc, 2-isopropyl-3-Δ^2-butenyl-cyclopentadienyl indium, di-(cyclopentadienyl)osmium, di-(4-n-nonyl-cyclopentadienyl)osmium, di-(2-ethenyl-cyclopentadienyl)osmium, (2-ethyl-cyclopentadienyl)-(3-n-propyl-cyclopentadienyl)osmium, di(cyclopentadienyl)ruthenium, di-(3-n-decyl-cyclopentadienyl)ruthenium, di-(4-(Δ^2-pentenyl)-cyclopentadienyl)ruthenium, (3-methyl-cyclopentadienyl)-(4-methyl-cyclopentadienyl)ruthenium, di(cyclopentadienyl)iron, di-(4-ethyl-cyclopentadienyl)iron, (3-methyl-cyclopentadienyl)-(4-ethylcyclopentadienyl)iron, tri(cyclopentadienyl)scandium, tri-(2,3-diethyl-cyclopentadienyl)scandium, (2-methyl-cyclopentadienyl)-di-(3-ethyl-cyclopentadienyl)scandium, 2-ethyl-cyclopentadienyl)-(3-ethyl-cyclopentadienyl)-(4-ethyl-cyclopentadienyl)scandium, tetra(cyclopentadienyl)dysprosium, tetra-(3-methyl-cyclopentadienyl)-dysprosium, and the like.

In addition, the R_1, R_2, R_3, R_4, and R_5 groups of the antiknock agents of our invention can be aryl radicals, such as, for example, phenyl, α-naphthyl, β-naphthyl, α-anthryl, β-anthryl, γ-anthryl, and the like, including the various monovalent radicals of such aromatics as indene, isoindene, acenaphthene, fluorene, phenanthrene, naphthacene, chrysene, pyrene, triphenylene, and the like.

Illustrative examples of aryl substituted cyclopentadienyl metal compounds comprising the antiknock ingredients of our invention include, for example, such compounds as 2-phenyl-cyclopentadienyl boron, 4-(α-naphthyl)-cyclopentadienyl boron, 2-(β-naphthyl)-cyclopentadienyl thallium, 3-methyl-4-phenyl-cyclopentadienyl thallium, 2,3-dimethyl-4-phenyl-cyclopentadienyl thallium, 3,4-diphenyl-cyclopentadienyl gallium, 3,5-diphenyl-cyclopentadienyl indium, di-(4-phenyl-cyclopentadienyl) osmium, (2-ethyl-cyclopentadienyl)-(3-phenyl-cyclopentadienyl)ruthenium, di-(4-phenyl-cyclopentadienyl)iron, and the like.

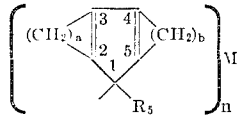
In addition, the R_1, R_2, R_3, R_4, and R_5 groups of the antiknock agents of our invention can be aralkyl radicals such as, for example, benzyl, α-phenyl-ethyl, β-phenyl-ethyl, α-phenyl-propyl, β-phenyl-propyl, γ-phenyl-propyl, α-phenyl-isopropyl, β-phenyl-isopropyl, α-phenyl-butyl, β-phenyl-butyl, γ-phenyl-butyl, δ-phenyl-butyl, α-phenyl-isobutyl, β-phenyl-isobutyl, γ-phenyl-isobutyl, α-phenyl-sec-butyl, β-phenyl-sec-butyl, γ-phenyl-sec-butyl, β-phenyl-t-butyl, α'-naphthyl-methyl, β'-naphthyl-methyl, α-(α'-naphthyl)-ethyl, α-(β'-naphthyl)-ethyl, β-(α'-naphthyl)-ethyl, β-(β'-naphthyl)-ethyl, α-(α'-naphthyl)-propyl, α-(β'-napthyl)-propyl, (α'-naphthyl)-propyl, β-(β'-naphthyl)-propyl, γ-(α'-naphthyl)-propyl, γ-(β'-naphthyl)-propyl, α-(α'-naphthyl)-isopropyl, α-(β'-naphthyl)-isopropyl, α-(α'-naphthyl)butyl, α-(β'-naphthyl)-butyl, β-(α'-naphthyl)-butyl, β-(β'-naphthyl)-butyl, γ-(α'-naphthyl)-butyl, γ-(β'-naphthyl)-butyl, δ-(α'-naphthyl)-butyl, δ-(β'-naphthyl)-butyl, α-(α'-naphthyl)-isobutyl, α-(β'-naphthyl)-isobutyl, β-(α'-naphthyl)-isobutyl, β-(β'-naphthyl)-isobutyl, γ-(α'-naphthyl)-isobutyl, γ-(β'-naphthyl)-isobutyl, α-(α'-naphthyl)-sec-butyl, α-(β'-naphthyl)-sec-butyl, β-(α'-naphthyl)-sec-butyl, β-(β'-naphthyl)-sec-butyl, γ-(α'-naphthyl)-sec-butyl, γ-(β'-naphthyl)-sec-butyl, β-(α'-naphthyl)-t-butyl, β-(β'-naphthyl)-t-butyl, the corresponding α'- and β'-naphthyl derivatives of n-amyl and the various positional isomers thereof such as, for example, said derivatives of 1-methyl-butyl, 2-methyl-butyl, 3-methyl-butyl, 1,1-dimethyl-propyl, 1,2-dimethyl-propyl, 2,2-dimethyl-propyl, 1-ethyl-propyl, and likewise said derivatives of the corresponding isomers of hexyl, heptyl, octyl, and the like, including eicosyl. Other such aralkyl derivatives of the compounds of our invention include the α'- and β'-, and γ'-anthryl derivatives of alkyl radicals, such as, for example, α'-anthryl-methyl, α-(β'-anthryl)-ethyl, β-(γ'-anthryl)-ethyl, α-(α'-anthryl)-butyl, δ-(β'-anthryl)-2-methyl-amyl, and the like, and the corresponding alkyl derivatives of phenanthrene, fluorene, acenaphthene, chrysene, pyrene, triphenylene, naphthacene, and the like.

Illustrative examples of aralkyl substituted cyclopentadienyl metal compounds comprising the antiknock ingredients of our invention include, for example, such compounds as di-(3-benzyl-cyclopentadienyl)beryllium, tri-(4-(α-phenylethyl)-cyclopentadienyl)yttrium, tri-(3-(β-phenylethyl-cyclopentadienyl)lanthanum, tri-(3,4-di-(α-phenyl-butyl)-cyclopentadienyl)chromium 2-benzyl-cyclopentadienyl aluminum, tetra-(3-benzyl-cyclopentadienyl)tin, tetra-(3-benzyl-cyclopentadienyl)lead, and the like.

In addition, the R_1, R_2, R_3, R_4, and R_5 groups of the antiknock agents of our invention can be alkaryl such as, for example, o-tolyl, m-tolyl, p-tolyl, o-ethylphenyl, m-ethylphenyl, p-ethylphenyl, o-n-propylphenyl, m-n-propylphenyl, p-n-propylphenyl, o-isopropylphenyl, m-isopropylphenyl, p-isopropylphenyl, 2-methyl-α-naphthyl, 3-methyl-α-naphthyl, 4-methyl-α-naphthyl, 5-methyl-α-naphthyl, 6-methyl-α-naphthyl, 7-methyl-α-naphthyl, 8-methyl-α-naphthyl, 1-ethyl-β-naphthyl, 3-ethyl-β-naphthyl, 4-ethyl-β-naphthyl, 5-ethyl-β-naphthyl, 6-ethyl-β-naphthyl, 7-ethyl-β-naphthyl, 8-ethyl-β-naphthyl, 2,3-dipropyl-α-naphthyl, 5,8-di-isopropyl-β-naphthyl, and the like.

Illustrative examples of alkaryl substituted cyclopentadienyl metal compounds comprising the antiknock ingredients of our invention include, for example, such compounds as di-(3-o-tolyl-cyclopentadienyl)calcium, di-(4-m-tolyl-cyclopentadienyl)strontium, tetra-(3-p-tolyl-cyclopentadienyl)titanium, di-(3-o-ethylphenyl-cyclopentadienyl)copper, 2-m-ethylphenyl-cyclopentadienyl silver, tetra-(4-p-ethylphenyl-cyclopentadienyl) germanium, and the like.

As hitherto indicated, the cyclopentadienyl moiety of the antiknock compounds of our invention can be directly bonded with at least one fused ring structure, thereby providing an organic ring-containing cyclopentadienyl moiety. The organic ring structure fused with the cyclopentadienyl moiety of the compounds of our invention can be alicyclic or aromatic. When this structure is alicyclic, there is provided a series of compounds which can be represented by the general formula

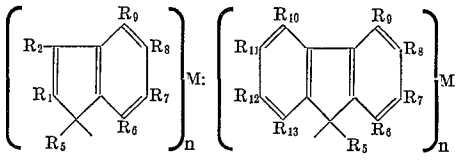


wherein a and b can be the same or different and are small whole integers including zero and excluding one, wherein n and M are as described heretofore, and wherein R_5 is selected from the class consisting of hydrogen and organic radicals, as described heretofore. Thus, when a is zero, each of the carbon atoms designated as 2 and 3 have attached thereto a monovalent radical selected from the class consisting of hydrogen and organic radicals. Furthermore, the monovalent radicals so attached can be the same or different. The same discussion applies to each of the carbon atoms designated as 4 and 5 when b is zero.

Illustrative examples of alicyclic ring-containing cyclopentadienyl metal compounds comprising the antiknock ingredients of our invention include, for example, such compounds as 4,5,6,7-tetrahydroindenyl thallium; 1,2,3,4,5,6,7,8-octahydrofluorenyl gallium; 3-methyl-4,5,6,7-tetrahydroindenyl indium, di-(4,5,6,7-tetrahydroindenyl) iron; di-(1,2,3,4,5,6,7,8-octahydrofluorenyl)osmium; di-

(4,5,6,7 - tetrahydroindenyl)ruthenium; (3-phenyl-cyclopentadienyl) - di - (4,5,6,7 - tetrahydroindenyl)scandium; and the like.

When the organic ring structure fused with the cyclopentadienyl moiety of the compounds of our invention is aromatic, there is provided a series of compounds which can be represented by the general formulae



wherein each of R_1, R_2, R_5, R_6, R_7, R_8, R_9, R_{10}, R_{11}, R_{12} and R_{13} can be the same or different and are selected from the class consisting of hydrogen and organic radicals, and wherein n and M are as described heretofore.

Illustrative examples of aromatic ring-containing cyclopentadienyl metal compounds comprising the antiknock ingredients of our invention include, for example, such compounds as di(indenyl) beryllium, di(fluorenyl) beryllium, di-(4,7-dimethyl indenyl) magnesium, di-(4-phenyl fluorenyl) magnesium, di(indenyl) calcium, di(fluorenyl) strontium, di-(3-methyl-4,6-diethyl indenyl) barium, di-(indenyl) osmium, di(fluorenyl) osmium, di(indenyl) ruthenium, di(fluorenyl) ruthenium, indenyl thallium, fluorenyl thallium, 1-methyl-8-phenyl fluorenyl thallium, tri(indenyl) scandium, tri-(2,4-diethyl indenyl) scandium, indenyl gallium, fluorenyl gallium, indenyl indium, fluorenyl indium, tetra(indenyl) dysprosium, and the like.

In addition, the metallic atom can have attached thereto different organic radicals, all of which do not have to be cyclopentadienyl moiety-containing radicals. Thus, for example, our fuel compositions can contain such materials as methyl-cyclopentadienyl iron, ethyl-cyclopentadienyl iron, propyl-cyclopentadienyl iron, isopropyl-cyclopentadienyl ruthenium, butyl-indenyl ruthenium, sec-butyl-fluorenyl ruthenium, isobutyl-3-methyl-cyclopentadienyl osmium, t - butyl - 5 - o - tolyl-fluorenyl osmium, phenyl - cyclopentadienyl barium, ethyl - di(cyclopentadienyl) scandium, diethyl-indenyl scandium, methylethyl-fluorenyl scandium, ethyl-tri(cyclopentadienyl) dysprosium, di(phenyl)-di(fluorenyl) dysprosium, tributyl-indenyl dysprosium, methylethyl-phenyl-cyclopentadienyl dysprosium, triethyl-cyclopentadienyl lead, and the like.

Certain polyvalent metals such as lead, tin, silicon, germanium, and the like, are capable of forming metal-to-metal bonds. In such instances the antiknock agents of our invention comprise polymetallic cyclopentadienyl moiety-containing compounds such as, for example, hexa-(cyclopentadienyl)dilead, hexa(indenyl)ditin, di(fluorenyl)-tetraethyl digermanium, diethyl-tetra(cyclopentadienyl)digermanium, octa(cyclopentadienyl)trisilicon, and the like.

General methods employed for preparing the metallic cyclopentadienyl moiety-containing compounds comprising the antiknock ingredients of our invention include the interaction of a cyclopentadienyl Grignard reagent or a cyclopentadienyl alkali metal compound with a salt of the desired metal. Reaction proceeds readily, and the products are easily recovered in high yield and purity because of the stability of the metallic cyclopentadienyl compounds. In certain instances we find that we can introduce the first cyclopentadienyl moiety by the use of the Grignard reagent, followed by introduction of additional cyclopentadienyl moieties by the use of the alkali metal compound. In the specific example which follows of one method of preparing a representative member of the compounds comprising antiknock ingredients of our invention, all parts and percentages are by weight.

Example

Di(cyclopentadienyl)iron.—A stirred reaction vessel provided with a reflux condenser and means for introducing liquid components was charged with 300 parts of anhydrous ethyl ether and 40 parts of magnesium metal. To this mixture was added 205 parts of ethyl bromide, the addition taking a period of approximately one hour, followed by the addition of 178 parts of cyclopentadiene. A solution of 90 parts of anhydrous ferric chloride in 200 parts of diethyl ether was then added to the reaction mixture over a period of approximately 30 minutes. The reaction mixture was then maintained at a reflux temperature in the order of 40° C. for a period of one hour. After cooling, the crude di(cyclopentadienyl) iron was isolated by adding an approximately 10 percent aqueous solution of ammonium chloride to the reaction mixture. The ether layer containing the desired product was separated and the ether removed by distillation. Forty-eight parts of crude product were obtained. The 48 parts of the crude product so obtained was recrystallized from ethyl alcohol solution and dried, yielding 26 parts of pure di(cyclopentadienyl) iron, amounting to an overall recovery of 25 percent. By analysis, this material was shown to contain 29.43 percent iron, while the formula $C_{10}H_{10}Fe$ requires 30.02 percent iron.

We have found that we can prepare typical compounds of our invention by utilizing the corresponding cyclopentadienyl moiety-containing Grignard reagent. Thus, for example, we can prepare cyclopentadienyl thallium by the interaction of cyclopentadienyl magnesium bromide and thallium iodide in accordance with the specific example described above. Therefore, by reacting indenyl magnesium bromide or chloride with such metallic halides as thallium iodide, bismuth chloride, osmium chloride, ruthenium chloride, gallium bromide, indium chloride, dysprosium chloride, and the like, we form the corresponding metallic indenyl compounds comprising the antiknock agents of our invention. Similarly, by reacting fluorenyl magnesium bromide or chloride with such metallic halides as boron chloride, cerium bromide, chromium chloride, cobalt chloride, nobium bromide, germanium chloride, iridium bromide, and the like, we form the corresponding metallic fluorenyl compounds comprising the antiknock agents of our invention. To prepare alkyl and aryl substituted cyclopentadienyl moiety-containing metallic compounds, we employ the corresponding alkyl or aryl substituted cyclopentadienyl moiety-containing Grignard reagent for reaction with the corresponding metallic halide. As heretofore indicated, we sometimes find it advantageous to employ the corresponding cyclopentadienyl moiety-containing alkali metal compound such as, for example, cyclopentadienyl lithium, indenyl lithium, fluorenyl sodium, and the like in the preparation of the compounds comprising the antiknock ingredients of our invention. Furthermore, in the preparation of certain of the metallic cyclopentadienyl moiety-containing compounds, we find it advantageous to introduce the first cyclopentadienyl moiety by the use of a cyclopentadienyl magnesium bromide, indenyl magnesium bromide, fluorenyl magnesium bromide, and the like, followed by the use of the aforementioned cyclopentadienyl moiety-containing alkali metal compounds to introduce additional cyclopentadienyl moieties into our antiknock compounds.

An advantage of the metallic cyclopentadienyl moiety-containing compounds is the effectiveness of such compounds in diverse hydrocarbon fuel types such as, for example, straight run hydrocarbons and processed hydrocarbons, including thermally crack, catalytically cracked, reformed, hydroformed, et cetera, hydrocarbons of the gasoline boiling range. Furthermore, we can employ the antiknock agents in fuels of widely varying sulfur contents.

To demonstrate the startling antiknock effectiveness of the metallic cyclopentadienyl moiety-containing compounds, four parts of di(cyclopentadienyl) iron was dissolved in 1300 parts of a representative petroleum hydrocarbon fuel and agitated, thereby forming a uniformly distributed hydrocarbon additive composition. The clear hydrocarbon fuel had a Research rating of 77.5 octane number. The resulting fuel mixture containing 8.53 parts of di(cyclopentadienyl) iron per gallon was compared with another blend of the same petroleum hydrocarbon fuel containing various concentrations of tetraethyllead. It was found that the di(cyclopentadienyl) iron-containing gasoline had an octane number of 91.7. In order to achieve the same octane number, it was necessary to employ 4.44 milliliters of tetraethyllead per gallon. Thus, iron as a cyclopentadienyl moiety-containing compound was 1.83 times more effective than lead as tetraethyllead.

Furthermore, cyclopentadienyl moiety-containing compounds can be successfully employed as antiknock additives to diverse commercially available fuels having wiedly differing chemical compositions with respect to hydrocarbon type and sulfur content. Thus, for example, we can employ cyclopentadienyl thallium in the following typical gasoline comprising the following component percentages: straight run, 51.4; catalytically cracked, 22.8; thermally cracked, 14.3; isopentane, 8.6; butane, 2.9; having a sulfur content of 0.162 percent; and having a clear Research octane number of 81.2, in amounts between about 0.03 and 8.0 grams of thallium per gallon to provide a fuel of superior antiknock quality.

Likewise, we can employ fluorenyl thallium in the following typical gasoline comprising the following component percentages: straight run, 61.0; catalytically cracked, 39.0; having a sulfur content of 0.168 percent, and having a clear Research octane number of 82.1, in antiknock quantities, that is, in amounts between about 0.03 and 8.0 grams of thallium per gallon to provide a fuel of superior antiknock quality.

Furthermore, we can employ 4,5,6,7-tetrahydroindenyl thallium in the following typical gasoline comprising the following component percentages: straight run, 45.1; catalytically cracked, 28.7; thermally reformed, 13.5; catalytic polymer, 8.7; butane, 4.0; having a sulfur content of 0.067 percent, and having a clear Research octane number of 81.5, in antiknock quantities, that is, in amounts between about 0.03 and 8.0 grams of thallium per gallon to provide a fuel of superior antiknock quality.

In addition, we can employ di-indenyl iron in the following typical gasoline comprising the following component percentages: catalytically cracked, 34.8; straight run, 29.1; thermally cracked, 25.2; hydroaromatic catalytically cracked, 10.9; having a sulfur content of 0.083 percent, and having a clear Research octane number of 83.9, in antiknock quantities, that is, in amounts between about 0.01 and 8.0 grams of iron per gallon to provide a fuel of superior antiknock quality.

Likewise, we can employ di-indenyl osmium in the following typical gasoline comprising the following component percentages: catalytically cracked, 60.6; straight run, 29.3; catalytically reformed, 10.1; having a sulfur content of 0.042 percent, and having a clear Research octane number of 85.4, in antiknock quantities, that is, in amounts between about 0.02 and 8.0 grams of osmium per gallon to provide a fuel of superior antiknock quality.

Furthermore, we can employ di-indenyl ruthenium in the following typical gasoline comprising the following component percentages: straight run, 63.0; thermally cracked, 37.0; having a sulfur content of 0.120 percent, and having a clear Research octane number of 81.6, in antiknock quantities, that is, in amounts between about 0.015 and 8.0 grams of ruthenium per gallon to provide a fuel of superior antiknock quality.

In addition, we can employ 3-methyl fluorenyl gallium in the following typical gasoline comprising the following component percentages: straight run, 32.7; catalytically cracked, 22.6; catalytically reformed, 22.7; thermally cracked, 19.8; butane, 2.2; having a sulfur content of 0.096 percent, and having a clear Research octane number of 82.1, in antiknock quantities, that is, in amounts between about 0.05 and 8.0 grams of gallium per gallon to provide a fuel of superior antiknock quality.

Likewise, we can employ 5-phenyl indenyl indium in the following typical gasoline comprising the following component percentages: catalytically cracked, 46.1; straight run, 27.4; thermally cracked and thermally reformed, 11.2; catalytic polymer, 9.1; butane, 6.2; having a sulfur content of 0.050 percent, and having a clear Research octane number of 81.7, in antiknock quantities, that is, in amounts between about 0.04 and 8.0 grams of indium per gallon to provide a fuel of superior antiknock quality.

Furthermore, we can employ tri-(2,4-diethyl cyclopentadienyl) scandium in the following typical gasoline comprising the following component percentages: catalytically cracked, 50.0; straight run, 40.0; catalytic polymer, 10.0; having a sulfur content of 0.036 percent, and having a clear Research octane number of 81.3 in antiknock quantities, that is, in amounts between about 0.02 and 8.0 grams of scandium per gallon to provide a fuel of superior antiknock quality.

In addition, we can employ tetra(cyclopentadienyl) dysprosium in the following typical gasoline comprising the following component percentages: catalytically cracked, 56.0; straight run, 18.0; thermally reformed, 17.1; catalytic polymer, 6.3; butane, 2.4; solvent oil, 0.2; having a sulfur content of 0.038 percent, and having a clear Research octane number of 85.0 in antiknock quantities, that is, in amounts between about 0.06 and 8.0 grams of dysprosium per gallon to provide a fuel of superior antiknock quality.

We also find it advantageous to employ other fuel additives old in the art in certain of the fuel compositions of the instant invention, which contain certain of the cyclopentadienyl moiety-containing compounds. Thus, for example, with certain of said compounds, we prefer to employ corrective agents, commonly known as scavengers, such as, for example, those disclosed in U.S. 1,592,954, 1,668,022, 2,364,921, 2,398,281, 2,479,900, 2,479,901, 2,479,902, 2,479,903, and 2,496,983. With certain other cyclopentadienyl moiety-containing fuel additives, we prefer to employ wear inhibitors such as, for example, those disclosed in U.S. 2,546,421 and 2,546,422. In addition to the foregoing, we find that antioxidant compositions can be successfully employed in our antiknock hydrocarbon fuel compositions as well as organic dyes and the like.

In general, we can employ in our improved fuel compositions cyclopentadienyl moiety-containing compounds in amounts from between about 0.01 and 8.0 grams of metal per gallon, which amount to from between about 0.93 and 740 pounds of metal per 1,000 barrels of gasoline. The specific amount of this cyclopentadienyl moiety-containing compound we employ is contingent upon the type of fuel, the specific compound, and the desired octane increase involved. However, in general, we prefer to employ from between about 0.1 and 4.6 grams of metal per gallon, which amount to from between about 9.3 and 427 pounds of metal per 1,000 barrels.

Other examples of the metallic cyclopentadienyl moiety-containing compounds which we have provided will be apparent, the specific examples enumerated herein being merely illustrative. Furthermore, other methods for their preparation will be apparent to those skilled in the art, and the foregoing example of preparation is presented merely to illustrate one method for their preparation.

Having thus described the novel antiknock compounds of our invention and having shown the advantages thereof and methods of employing them, we do not intend that our invention be limited except within the scope of the following claims.

We claim:

1. A compound having the formula R—M wherein R is a cyclopentadienyl hydrocarbon group and M is a Group III–A element having an atomic number of at least 31, the element M being bonded to a cyclopentadienyl ring of the cyclopentadienyl group, said cyclopentadienyl group containing from 5 to 17 carbon atoms.

2. Cyclopentadienyl thallium.

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