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ANTIKNOCK COMPOSITIONS AND MOTOR FUELS CONTAINING THEM

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This invention relates to new and improved antiknock compositions which are combinations of dicyclopentadienyl iron compounds and cyclopentadienyl nickel nitrosyl compounds which are soluble in hydrocarbon motor fuels, are inductible with such fuels in spark-ignition engines, and which cooperate synergistically in such motor fuels to improve the antiknock quality of the fuels.

Tetraalkyl lead antiknock compounds are widely employed to provide high quality fuels for spark-ignition engines. A disadvantage in their use, however, owing to their loss in efficiency with increasing dosage, is the rapid rise in the cost of enhancing fuel octane quality as the required amount of antiknock compound increases. Other organometal compounds have also been proposed for this use, a particularly notable class involving metals of the first transition series chemically combined in such forms as metal carbonyls, dicyclopentadienyl metal compounds, cyclopentadienyl metal carbonyls, cyclopentadienyl metal nitrosyls, and similarly constituted molecules. Like the tetraalkyl lead compounds, these organometal compounds also tend to diminish in antiknock effectiveness with increasing concentration.

To circumvent this trend through the use of mixtures of different organometal compounds has, in general, not been feasible. Such mixtures tend to show one of three types of behavior, generally not predictable in advance: (1) The combination of metals is quite often less effective than the individual components. (2) The combination provides improved results, that is, greater than expected, sometimes, in rare instances, even greater than additive, with the largest beneficial effects usually obtained when one of the metal components is present in very low concentration relative both to the fuel and the other metal component. In such unusul situation, the synergistically interacting antiknock metals are invariably of two different groups, quite dissimilar in the nature and character of the metal, e.g. Mn and Pb, or Fe and Pb. Also, the compounds usually differ in the type and constitution of the groups bonded to the antiknock metal, e.g. carbonyl and cyclopentadienyl groups of transition metal compounds and alkyl groups of leaded antiknock compounds. (3) The components of the mixture function as an average unit, paralleling the behavior of the individual components, but rarely ever as effective as the most effective single component alone. In this third situation, which commonly occurs when the substances involved are analogous or closely related in form and structure, the fuel response depends largely on the total metal concentration (as it does with single component antiknock agents) and, typically, the effectiveness of the mixture decreases with increasing total metal concentration. Thus, at any total metal concentration, the overall result is less than additive and normally is governed by the relation, $Y(n)=f_1d_1+f_2d_2+ \ldots fm\ dm$, where $Y(n)$ is the improvement in fuel antiknock quality obtained at total metal concentration n, f_1, f_2 and fm are the fractions by weight of each of the m number of organometal components present in the fuel and d_1, d_2 and dm are the improvements in antiknock quality obtained with each of the organometal compounds alone at concentration n.

Brown et al., in U.S. Patent 3,006,742, disclose as antiknock compounds various organometallic compounds

which contain both a cyclomatic group and a different functional group attached to the metal, and which do not possess a "sandwich" structure. They indicate that superior antiknock and antiwear properties are obtained with mixtures of iron compounds and zinc compounds of their invention, and that other beneficial mixtures include those of iron compounds and nickel compounds of their invention. However, it has been found that not all organoiron compounds will so act with all organonickel compounds or even with cyclopentadienyl nickel nitrosyl compounds, but that the nature of the organic radicals attached to the metal, particularly to iron, and the molecular structure of the organometal compounds seriously affects the results, whereby it cannot be predicted that organometal molecules of different structures will act in the same way.

An object of this invention is to provide new highly effective antiknock compositions for fuels for spark-ignition engines. Another object is to provide new synergistically interacting combinations of readily available organometal antiknock compounds. Still another object is to provide new combinations of lead-free organometal antiknock compounds, which, when used in conjunction with tetraalkyl lead antiknock compounds, provide improved antiknock effects not obtainable through the use of either the individual components of the mixture or additional quantities of tetraalkyl lead. A further object is to provide new fuel compositions, having improved resistance to knock, comprising a hydrocarbon fuel for spark-ignition engines and new synergistically interacting organometal antiknock compounds. Other objects are to advance the art. Still other objects will appear hereinafter.

The above and other objects may be accomplished by this invention wherein there are provided novel antiknock compositions and new and improved motor fuels containing them, all as more fully described hereinafter.

In its broad aspects, this invention provides an antiknock composition comprising

(A) a binary mixture of iron and nickel antiknock compounds consisting essentially of
  (a) about 85% to about 50% by weight of at least one member of the group consisting of dicyclopentadienyl iron and substituted-dicyclopentadienyl iron in which the substituents consist of at least one alkyl radical of 1 to 2 carbon atoms, and
  (b) about 15% to about 50% by weight of at least one member of the group consisting of cyclopentadienyl nickel nitrosyl and substituted-cyclopentadienyl nickel nitrosyl in which the substituents consist of at least one alkyl radical of 1 to 2 carbon atoms.

Other features of this invention include antiknock compositions comprising the aforesaid binary mixtures and tetraalkyl lead antiknock compositions, and motor fuels for spark-ignition engines which consist essentially of liquid hydrocarbons boiling in the gasoline range and which contain such antiknock compositions.

This invention is based on the discovery that the above particularly defined compounds of iron and nickel, when used in the defined combinations in hydrocarbon motor fuels for spark-ignition engines, significantly enhance the octane quality of said fuels. The combined effect of the compounds is synergistic and essentially independent of the presence of conventionally employed tetraalkyl lead antiknock compounds or other additives normally associated with the use of commercial motor fuels for spark-ignition engines.

The beneficial interaction of these compounds of iron and nickel is not understood in terms of known theories of antiknock action. Nevertheless, the improved antiknock results, provided by the defined combinations of

the specified compounds of iron and nickel, are believed unexpected and unobvious since (a) other closely related iron antiknock compounds, for example butadiene iron tricarbonyl, cycloheptatriene iron tricarbonyl (Ihrman et al., U.S. Patent 3,037,999), and iron pentacarbonyl, either do not interact significantly with the cyclopentadienyl nickel nitrosyl component or are much less effective than the dicyclopentadienyl sandwich form of iron as the cooperating agent for the nickel nitrosyl compounds; (b) replacing the nickel component by another transition metal antiknock compound of similar character, such as methylcyclopentadienyl manganese tricarbonyl, results in either no or only relatively weak synergistic interaction; and (c) similarly, replacing the dicyclopentadienyl iron component by another transition metal antiknock compound, for example methylcyclopentadienyl manganese tricarbonyl, provides little or no synergistic antiknock effect.

Thus, the dicyclopentadienyl iron compounds and the cyclopentadienyl nickel nitrosyl compounds seem to be unique in their ability to cooperate so effectively with one other. Surprisingly too, such cooperative effect is not limited to certain low ratios of one metal to the other or to any particularly low metal concentration in the fuel, which conditions of concentration usually characterize synergistic organometal combinations of the prior art. In fact, the combinations of this invention show maximum synergistic interaction, providing the greatest increases in the octane quality of the fuel, when both iron and nickel are present in about equal amounts. Also, the improvements (obtained in accordance with this invention) are particularly significant in leaded gasolines, since such improvements often cannot be matched by the addition of comparable proportions of tetraalkyl lead antiknock compound. With fuels already containing substantial quantities of tetraalkyl lead, it is often impossible (or, practically speaking, not permissible to attempt) to attain, with additional tetraalkyl lead, the high level of knock resistance provided by the iron-nickel combinations of this invention in such leaded gasolines.

The dicyclopentadienyl iron compounds which may be employed in this invention consist of dicyclopentadienyl iron, substituted-dicyclopentadienyl iron in which the substituents consist of at least one alkyl radical of 1 to 2 carbon atoms, and mixtures of any two or more thereof. Suitable alkyl-substituted-dicyclopentadienyl iron compounds include cyclopentadienyl(methylcyclopentadienyl) iron, cyclopentadienyl(ethylcyclopentadienyl) iron, bis-(methylcyclopentadienyl) iron, bis-(ethylcyclopentadienyl) iron, methylcyclopentadienyl(ethylcyclopentadienyl) iron, bis-(1,2-dimethylcyclopentadienyl) iron, and bis-(1-methyl-3-ethylcyclopentadienyl) iron. Such iron compounds are well known and may be prepared by the methods described by Pauson in U.S. Patent 2,680,756, Arimoto in U.S. Patent 2,804,468, and in British Patents 733,129 and 763,550. Dicyclopentadienyl iron and bis-(methylcyclopentadienyl) iron are preferred.

The cyclopentadienyl nickel nitrosyl compounds which may be used in accordance with this invention consist of cyclopentadienyl nickel nitrosyl substituted-cyclopentadienyl nickel nitrosyl in which the substituents consist of at least one alkyl radical of 1 to 2 carbon atoms and mixtures of any two or more thereof. Suitable alkyl-substituted-cyclopentadienyl nickel nitrosyl compounds are exemplified by methylcyclopentadienyl nickel nitrosyl, ethylcyclopentadienyl nickel nitrosyl, 1,2-dimethylcyclopentadienyl nickel nitrosyl, 1,3-dimethylcyclopentadienyl nickel nitrosyl, and 1-methyl-3-ethylcyclopentadienyl nickel nitrosyl. Cyclopentadienyl nickel nitrosyl and methylcyclopentadienyl nickel nitrosyl are preferred. Such nickel nitrosyls are disclosed in British Patent 882,747 and by Brown et al. in U.S. Patents 2,818,416 and 3,006,742.

The dicyclopentadienyl iron compounds and the cyclopentadienyl nickel nitrosyl compounds of the foregoing classes individually and together are readily soluble in normally liquid hydrocarbon solvents such as gasoline, kerosene, toluene and xylene, and other common organic solvents, and are readily blendable therewith. They are stable under normal atmospheric conditions and are sufficiently stable and volatile under the operating conditions of spark-ignition engines so that they are inducted into such engines with the main fuel charge by the conventional carburetion and fuel injection techniques.

The antiknock compositions of this invention are useful in motor fuels for spark-ignition engines which consist essentially of liquid hydrocarbons boiling in the gasoline range. Usually, such motor fuels are those which are commonly referred to as gasoline. Such fuels are generally mixtures of hydrocarbons, usually blends of various hydrocarbon fractions composed of paraffinic, olefinic, cycloaliphatic and aromatic hydrocarbons, including such fractions and refinery products obtained by distillation, cracking, reforming, alkylation and polymerization processes. The gasolines normally have an initial boiling point in the range 70° F. to 100° F. and a final boiling point in the range 330° F. to 440° F. Many typical commercial automotive gasolines boil from 80° F. to 430° F. The motor fuels for the present purpose may be clear, i.e. unleaded, or may contain tetraalkyl lead antiknock compounds. The motor fuels also may contain other additives normally associated with the finished commercial fuels for present day spark-ignition internal combustion engines.

Normally, the binary mixtures of the antiknock compositions will consist essentially of from about 85% to about 50% by weight of one or more of the dicyclopentadienyl iron compounds and from about 15% to about 50% by weight of the cyclopentadienyl nickel nitrosyl compounds, preferably from about 75% to about 50% of the dicyclopentadienyl iron compounds and from about 25% to about 50% of the cyclopentadienyl nickel nitrosyl compounds. Such iron and nickel compounds may be added to the motor fuel separately, or may be handled and added to the fuel as a mixture. For purposes of convenience, it will generally be desirable to dissolve the binary mixture in a concentration of from about 20% to about 80% by weight in a normally liquid hydrocarbon solvent, such as kerosene, toluene, xylene, and the like and employ such concentrated solutions as the antiknock compositions.

Normally, the iron and nickel compounds will be added to the motor fuel in a proportion which will provide from about .01 to about 2 grams of the metal, Fe and Ni combined, for each gallon of the motor fuel, preferably from about 0.15 to about 1.5 grams of metal.

The binary mixture of dicyclopentadienyl iron compounds and cyclopentadienyl nickel nitrosyl compounds may be used in conjunction with tetraalkyl lead antiknock compounds. For this purpose, the binary mixture may be mixed with tetraalkyl lead antiknock compositions to provide antiknock compositions containing both the binary mixture and the tetraalkyl lead antiknock compound. In such case, the distribution of metals will be such that for each part by weight of lead there will be from about 0.025 to about 1 part of nickel and iron combined, preferably from about 0.1 to about 0.5 part of nickel and iron combined. In the motor fuels, wherein the binary mixture is employed in combination with a tetraalkyl lead antiknock compound, the tetraalkyl lead will be in a proportion to provide from about 1 to about 4.23 grams of lead per gallon of fuel and the binary mixture will be in a proportion to provide from about 0.1 to about 1 gram of nickel and iron combined for each gallon of fuel, preferably from about 0.3 to about 0.75 gram of nickel and iron combined.

The tetraalkyl lead compound, which may be employed in conjunction with the binary mixture of iron and nickel compounds, may be any of those known to the antiknock

art. Usually, the tetraalkyl lead compound will be a tetraloweralkyl lead, such as tetramethyl lead, tetraethyl lead (TEL), trimethyl ethyl lead, dimethyl diethyl lead, triethyl methyl lead, tetraisopropyl lead, and the like, and mixtures of any two or more thereof. Preferably, the tetraalkyl lead antiknock compounds will be those in which each alkyl group contains 1 to 2 carbon atoms, i.e. is selected from methyl and ethyl groups.

The tetraalkyl lead antiknock compounds are commonly employed in conjunction with one or more polyhalohydrocarbon lead scavengers. Usually, such scavengers are volatile halohydrocarbons of 2 to 8 carbon atoms which contain 2 to 3 halogen atoms of atomic numbers 17–35 and normally boil below about 250° C. Preferably, the scavenger will be a polyhaloalkane which consists of 2 carbon atoms, 2–3 halogen atoms of atomic numbers 17–35, and the rest hydrogen atoms, particularly ethylene dibromide, ethylene dichloride, and mixtures thereof. Such scavengers may be used with the binary mixtures of dicyclopentadienyl iron compounds and cyclopentadienyl nickel nitrosyl compounds and with mixtures thereof with tetraalkyl lead antiknock compounds. The scavenger will be employed in amounts furnishing 0.5 to about 2.5 theories of halogen for each atom of metal in the antiknock compounds, preferably from about 1 to about 1.5 theories of halogen. Also, preferably for automotive use, there will be employed about 0.5 theory of bromine, e.g. as ethylene dibromide, per atom of metal and about 1 theory of chlorine, e.g. as ethylene dichloride, per atom of metal. One theory of halogen corresponds to 3 atoms for each atom of Fe and 2 atoms for each atom of each of Ni and Pb. The antiknock compositions may also, as is conventional with tetraalkyl lead, contain an identifying dye; a solvent oil, such as kerosene or toluene; and other conventional additives, such as metal deactivators, antioxidants, antirust agents, antiicing agents, and antipreignition agents.

Accordingly, this invention includes, as antiknock compositions mixtures of the binary mixtures with tetraalkyl lead antiknock compounds, scavengers for the metals, and other conventional components of tetraalkyl lead antiknock compositions, preferably as concentrated solutions in normally liquid hydrocarbon solvents.

In order to more clearly illustrate this invention, preferred modes of carrying it into effect, and the advantageous results to be obtained thereby, the following examples are given in which the parts and proportions are by weight, except where specifically indicated otherwise.

Example 1

The base fuel employed is a regular grade, full-boiling, automotive gasoline having the following characteristics.

Composition:

Aromatic hydrocarbons, vol. percent	10
Olefinic hydrocarbons, vol. percent	4
Saturated hydrocarbons, vol. percent	86

ASTM distillation:

10% evap., ° F.	175
50% evap., ° F.	222
90% evap., ° F.	287

Octane rating, ASTM Research Method:

Clear fuel, O.N.	84.0
Plus 1 ml. TEL/gal.	92.0
Plus 3 ml. TEL/gal.	96.0

To separate portions of the unleaded base gasoline are added the antiknock compounds and the combinations thereof in the amounts described in the Table 1 below. The results are expressed in terms of the observed (Obs.) and the expected (Exp.) increases in the Research Method (F–1) octane number of the gasoline, the difference between the observed and expected (Obs.-Exp.) increases in knock resistance, and the percent increase this represents over the expected value (Percent over Exp.). The expected increase is calculated by the expression, $Y(n)=f_1d_1+f_2d_2$, where $Y(n)$ is the increase in octane rating predicted for the Fe plus Ni combination at total metal concentraiton n; f_1 is the weight fraction of Fe, and f_2 is the weight fraction of Ni in the mixture; and d_1 is the increase obtained with Fe alone, and d_2 the increase with Ni alone, each at concentration n.

The synergistic effect is exemplified at two levels of total metal concentration, 0.3 gram/gal. and 1.5 grams/gal. of the gasoline. Also, comparison is made of the effectiveness of Fe as dicyclopentadienyl iron (test 3), Fe as cycloheptatriene iron tricarbonyl (test 10), and Mn as methylcyclopentadienyl manganese tricarbonyl (test 5), each as the cooperating agent for the nickel compound.

TABLE 1.—OCTANE BENEFIT WITH DICYCLOPENTADIENYL IRON AND CYCLOPENTADIENYL NICKEL NITROSYL

[A. Fe and Ni versus Mn and Ni]

Test	Metal Concentration (0.3 g./gal. total)		Increase in Octane Number			
	Fe	Ni	Obs.	Exp.	Obs.-Exp.	Percent over Exp.
1	0.3		4.8			
2		0.3	3.6			
3	0.15	0.15	5.2	4.2	1.0	24
	Mn	Ni				
4	0.3		5.2			
2		0.3	3.6			
5	0.15	0.15	4.8	4.4	0.4	9

[B. Comparison of dicyclopentadienyl iron (I) and cycloheptatriene iron carbonyl (II) as the cooperative antiknock with cyclopentadienyl nickel nitrosyl]

Test	Metal Concentration (1.5 g./gal. total)		Increase in Octane Number			
	Fe	Ni	Obs.	Exp.	Obs.-Exp.	Percent over Exp.
6	1.5 (I)		9.7			
7		1.5	7.2			
8	1.0 (I)	0.5	9.8	8.9	0.7	8
9	1.5 (II)		9.9			
7		1.5	7.2			
10	1.0 (II)	0.5	7.9	9.0	−1.1	−12

Table 1, under A, shows that the combination of dicyclopentadienyl iron and cyclopentadienyl nickel nitrosyl is synergistic, the increase in octane number being nearly 25% greater than expected, and is also more than twice as effective as the combination of manganese and nickel (9% increase).

In additional comparative tests with the same base fuel, it was determined that there is required 0.47 gram Pb/gal. as tetraethyl lead to match the 5.2 octane number increase obtained with the total 0.3 gram metal (Fe plus Ni) per gal. in test 3, which attests to the significance and substantial character of the antiknock benefits provided by the iron and nickel cooperative antiknock combination of this invention.

Table 1, under B, shows again that dicyclopentadienyl iron and cyclopentadienyl nickel nitrosyl interact synergistically to improve fuel knock resistance, and further that the cooperating effect is not inherent in all iron compounds. In fact, the cycloheptatriene iron tricarbonyl and the cyclopentadienyl nickel nitrosyl tend to be strongly antagonistic. Again, as a point of reference, 1.85 grams Pb as tetraethyl lead are needed to provide the 9.8 octane number increase given by the 1.5 grams total Fe plus Ni in each gallon of the fuel.

Example 2

Tetraethyl lead "Motor Mix" formulation (a blend of 61.4% tetraethyl lead, 17.86% ethylene dibromide,

18.81% ethylene dichloride, and 1.88% kerosene) is blended into a portion of the base gasoline described in Example 1 in an amount corresponding to 1.0 gram Pb/gal., providing 1.0 theory of chlorine as ethylene dichloride and 0.5 theory of bromine as ethylene dibromide, and raising the Research Method octane rating to 92.0. Iron, as dicyclopentadienyl iron, and nickel, as cyclopentadienyl nickel nitrosyl, are blended into this leaded fuel in the tabulated quantities. The results are shown in Table 2.

TABLE 2.—SYNERGISTIC ANTIKNOCK EFFECT OF Fe AND Ni IN LEADED GASOLINE (1 GRAM Pb/GAL.)

Test	Metal Concentration		Increase in Octane Number			
	Fe	Ni	Obs.	Exp.	Obs.-Exp.	Percent over Exp.
11	0.30		1.8			
12		0.30	0.8			
13	0.20	0.10	2.0	1.6	0.4	25
14	0.15	0.15	2.2	1.5	0.7	47
15	0.60		3.0			
16		0.60	1.1			
17	0.40	0.20	3.0	2.4	0.6	25
18	0.30	0.30	3.1	2.2	0.9	41

Further tests established that, to match the 2.2 octane number increase of test 14, there is required 0.9 gram Pb as tetraethyl lead in place of the 0.3 gram Fe plus Ni total per gallon of the fuel. Also, to match the 3.1 octane number increase of test 18, there is needed 1.3 grams Pb as tetraethyl lead. These results again illustrate the high potency of the combination of the compounds of this invention to raise the octane number of motor gasoline.

Example 3

The base gasoline described in Example 1 is leaded with tetraethyl lead "Motor Mix" to contain 3.0 grams Pb/gal., thereby raising the Research Method octane number to 96.0. Dicyclopentadienyl iron or (a) butadiene iron tricarbonyl and cyclopentadienyl nickel nitrosyl are added in quantities corresponding to the metal concentrations shown below. Representative results are shown in Table 3.

TABLE 3.—SYNERGISTIC ANTIKNOCK EFFECT OF Fe AND Ni IN LEADED GASOLINE (3 GRAMS Pb/GAL.)

Test	Metal Concentration		Increase in Octane Number			
	Fe	Ni	Obs.	Exp.	Obs.-Exp.	Percent over Exp.
19	0.15		1.8			
20		0.15	1.0			
21	0.125	0.025	2.1	1.6	0.5	31
22	0.10	0.05	2.2	1.5	0.7	47
23	0.30		2.2			
24		0.30	1.9			
25	0.25	0.05	2.5	2.2	0.3	14
26	0.15	0.15	2.6	2.1	0.5	24
27	0.60		3.1			
28		0.60	2.6			
29	0.40	0.20	3.2	3.0	0.2	7
30	0.30	0.30	3.4	2.8	0.6	21
31	0.30 (a)		1.1			
32	0.25 (a)	0.05	1.3	1.2	0.1	6
33	0.20 (a)	0.10	1.3	1.4	−0.1	−5

In each test representing a combination of this invention, the observed octane number increase is greater than that obtained with either one of the additives alone, and is significantly greater than expected on the basis of the known relationships for mixtures of analogous and closely related antiknock structures. Also, it should be noted that, to match the antiknock increases of tests 22, 26 and 30 in this leaded base fuel, there would be required additional increments of tetraethyl lead amounting to 2.6 grams Pb, about 3.4 grams Pb, and over 4.5 grams Pb per gallon of fuel, respectively. Also, tests 31–33, as compared with tests 23–26, show that replacing dicyclopentadienyl iron with another closely related organo-iron antiknock compound, butadiene iron tricarbonyl, does not produce the advantageous results of this invention, but produces significantly inferior results.

That the synergistic interaction of the iron and nickel compounds of this invention is unobvious, is further indicated by the comparative testing of dicyclopentadienyl iron and methylcyclopentadienyl manganese tricarbonyl in the same leaded fuel. At a concentration of 0.30 gram metal/gal., the Mn compound raises the octane rating 2.5 units, the Fe compound 2.2 units. The combination of these two compounds, in equal metal concentrations of 0.15 gram/gal. each, gives a 2.3 unit increase, which is very close to the expected value of 2.35.

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 described therein. On the other hand, it will be readily apparent to those skilled in the art that, subject to the limitations set forth in the general description, various modifications can be made in the materials and proportions employed without departing from the spirit or scope of this invention.

From the foregoing description, it will be apparent that this invention provides novel antiknock compositions comprising mixtures of limited classes of dicyclopentadienyl iron compounds and of cyclopentadienyl nickel nitrosyl compounds in limited proportions, in which combinations the iron and nickel compounds cooperate synergistically in leaded and in unleaded motor fuels to greatly improve the antiknock quality of the motor fuels. By the use of such combination of such iron and nickel compounds, it is possible to obtain motor fuels of high antiknock properties which could not be obtained by the use of the conventional tetraalkyl lead antiknock compounds except at prohibitive cost. Accordingly, it will be apparent that this invention constitutes a valuable contribution to and advance in the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. An antiknock composition which consists essentially of

(A) a binary mixture of iron and nickel antiknock compounds consisting essentially of

(a) about 85% to about 50% by weight of at least one member of the group consisting of dicyclopentadienyl iron and substituted-dicyclopentadienyl iron in which the substituents consist of one to two alkyl radicals of 1 to 2 carbon atoms, and

(b) about 15% to about 50% by weight of at least one member of the group consisting of cyclopentadienyl nickel nitrosyl and substituted-cyclopentadienyl nickel nitrosyl in which the substituents consist of one to two alkyl radicals of 1 to 2 carbon atoms.

2. An antiknock composition which consists essentially of

(A) a binary mixture of iron and nickel antiknock compounds consisting essentially of

(a) about 75% to about 50% by weight of dicyclopentadienyl iron, and

(b) about 25% to about 50% by weight of cyclopentadienyl nickel nitrosyl.

3. An antiknock composition which consists essentially of

(A) a binary mixture of iron and nickel antiknock compounds in an amount to provide from about 0.025 to about 1.0 part by weight of iron and nickel combined, said binary mixture consisting essentially of

(a) about 85% to about 50% by weight of at least one member of the group consisting of dicyclopentadienyl iron and substituted-dicyclopentadienyl iron in which the substituents con-

sist of one to two alkyl radicals of 1 to 2 carbon atoms, and

(b) about 15% to about 50% by weight of at least one member of the group consisting of cyclopentadienyl nickel nitrosyl and substituted-cyclopentadienyl nickel nitrosyl in which the substituents consist of one to two alkyl radicals of 1 to 2 carbon atoms; and

(B) a tetraalkyl lead antiknock compound in an amount to provide about 1 part by weight of lead.

4. An antiknock composition which consists essentially of

(A) a binary mixture of iron and nickel antiknock compounds in an amount to provide from about 0.1 to about 0.5 part by weight of iron and nickel combined, said binary mixture consisting essentially of

(a) about 85% to about 50% by weight of at least one member of the group consisting of dicyclopentadienyl iron and substituted-dicyclopentadienyl iron in which the substituents consist of one to two alkyl radicals of 1 to 2 carbon atoms, and

(b) about 15% to about 50% by weight of at least one member of the group consisting of cyclopentadienyl nickel nitrosyl and substituted-cyclopentadienyl nickel nitrosyl in which the substituents consist of one to two alkyl radicals of 1 to 2 carbon atoms; and

(B) a tetraalkyl lead antiknock compound in which each alkyl group contains 1 to 2 carbon atoms in an amount to provide about 1 part by weight of lead.

5. An antiknock composition which consists essentially of

(A) a binary mixture of iron and nickel antiknock compounds in an amount to provide from about 0.1 to about 0.5 part by weight of iron and nickel combined, said binary mixture consisting essentially of

(a) about 85% to about 50% by weight of dicyclopentadienyl iron, and

(b) about 15% to about 50% by weight of cyclopentadienyl nickel nitrosyl; and

(B) a tetraalkyl lead antiknock compound in which each alkyl group contains 1 to 2 carbon atoms in an amount to provide about 1 part by weight of lead.

6. An antiknock composition which consists essentially of

(A) a binary mixture of iron and nickel antiknock compounds in an amount to provide from about 0.025 to about 1.0 part by weight of iron and nickel combined, said binary mixture consisting essentially of

(a) about 85% to about 50% by weight of at least one member of the group consisting of dicyclopentadienyl iron and substituted-dicyclopentadienyl iron in which the substituents consist of one to two alkyl radicals of 1 to 2 carbon atoms, and

(b) about 15% to about 50% by weight of at least one member of the group consisting of cyclopentadienyl nickel nitrosyl and substituted-cyclopentadienyl nickel nitrosyl in which the substituents consist of one to two alkyl radicals of 1 to 2 carbon atoms;

(B) a tetraalkyl lead antiknock compound in an amount to provide about 1 part by weight of lead; and

(C) from 0.5 to about 2.5 theories, based on the metals, of at least 1 polyhalohydrocarbon lead scavenger.

7. An antiknock composition which consists essentially of

(A) a binary mixture of iron and nickel antiknock compounds in an amount to provide from about 0.1 to about 0.5 part by weight of iron and nickel combined, said binary mixture consisting essentially of

(a) about 75% to about 50% by weight of at least one member of the group consisting of dicyclopentadienyl iron and substituted-dicyclopentadienyl iron in which the substituents consist of one to two alkyl radicals of 1 to 2 carbon atoms, and

(b) about 25% to about 50% by weight of at least one member of the group consisting of cyclopentadienyl nickel nitrosyl and substituted-cyclopentadienyl nickel nitrosyl in which the substituents consist of one to two alkyl radicals of 1 to 2 carbon atoms; and

(B) a tetraalkyl lead antiknock compound in which each alkyl group contains 1 to 2 carbon atoms in an amount to provide about 1 part by weight of lead; and

(C) from about 1 to about 2.5 theories, based on the metals, of at least 1 polyhaloalkane lead scavenger which consists of 2 carbon atoms, 2–3 halogen atoms of atomic numbers 17–35, and the rest hydrogen atoms.

8. An antiknock composition which consists essentially of

(A) a binary mixture of iron and nickel antiknock compounds consisting essentially of

(a) about 85% to about 50% by weight of at least one member of the group consisting of dicyclopentadienyl iron and substituted-dicyclopentadienyl iron in which the substitutents consist of one to two alkyl radicals of 1 to 2 carbon atoms, and

(b) about 15% to about 50% by weight of at least one member of the group consisting of cyclopentadienyl nickel nitrosyl and substituted-cyclopentadienyl nickel nitrosyl in which the substituents consist of one to two alkyl radicals of 1 to 2 carbon atoms; and

(D) a normally liquid hydrocarbon solvent in an amount sufficient to provide a solution containing said antiknock compounds in a concentration of from about 20% to about 80% by weight.

9. An antiknock composition which consists essentially of

(A) a binary mixture of iron and nickel antiknock compounds consisting essentially of

(a) about 75% to about 50% by weight of dicyclopentadienyl iron, and

(b) about 25% to about 50% by weight of cyclopentadienyl nickel nitrosyl; and

(D) a normally liquid hydrocarbon solvent in an amount sufficient to provide a solution containing said antiknock compounds in a concentration of from about 20% to about 80% by weight.

10. An antiknock composition which consists essentially of

(A) a binary mixture of iron and nickel antiknock compounds in an amount to provide from about 0.025 to about 1.0 part by weight of iron and nickel combined, said binary mixture consisting essentially of

(a) about 85% to about 50% by weight of at least one member of the group consisting of dicyclopentadienyl iron and substituted-dicyclopentadienyl iron in which the substituents consist of one to two alkyl radicals of 1 to 2 carbon atoms, and

(b) about 15% to about 50% by weight of at least one member of the group consisting of cyclopentadienyl nickel nitrosyl and substituted-cyclopentadienyl nickel nitrosyl in which the substituents consist of one to two alkyl radicals of 1 to 2 carbon atoms;

(B) a tetraalkyl lead antiknock compound in an amount to provide about 1 part by weight of lead;

(C) from 0.5 to about 2.5 theories, based on the metals,

of at least 1 polyhalohydrocarbon lead scavenger; and

(D) a normally liquid hydrocarbon solvent in an amount sufficient to provide a solution containing said antiknock compounds in a concentration of from about 20% to about 80% by weight.

11. A motor fuel for spark ignition engines which consists essentially of liquid hydrocarbons boiling in the gasoline range and which contains

(A) a binary mixture of iron and nickel antiknock compounds in an amount to provide a total of from 0.1 to about 2 grams of metal per gallon of said fuel, said binary mixture consisting essentially of

(a) about 85% to about 50% by weight of at least one member of the group consisting of dicyclopentadienyl iron and substituted-dicyclopentadienyl iron in which the substituents consist of one to two alkyl radicals of 1 to 2 carbon atoms, and

(b) about 15% to about 50% by weight of at least one member of the group consisting of cyclopentadienyl nickel nitrosyl and substituted-cyclopentadienyl nickel nitrosyl in which the substituents consist of one to two alkyl radicals of 1 to 2 carbon atoms.

12. A motor fuel for spark ignition engines which consists essentially of liquid hydrocarbons boiling in the gasoline range and which contains

(A) a binary mixture of iron and nickel antiknock compounds in an amount to provide a total of from 0.1 to about 2 grams of metal per gallon of said fuel, said binary mixture consisting essentially of

(a) about 75% to about 50% by weight of dicyclopentadienyl iron, and

(b) about 25% to about 50% by weight of cyclopentadienyl nickel nitrosyl.

13. A motor fuel for spark ignition engines which consists essentially of liquid hydrocarbons boiling in the gasoline range and

(A) a binary mixture of iron and nickel antiknock compounds in an amount to provide a total of from 0.1 to about 1 gram of metal per gallon of said fuel, said binary mixture consisting essentially of

(a) about 85% to about 50% by weight of at least one member of the group consisting of dicyclopentadienyl iron and substituted-dicyclopentadienyl iron in which the substituents consist of one to two alkyl radicals of 1 to 2 carbon atoms, and

(b) about 15% to about 50% by weight of at least one member of the group consisting of cyclopentadienyl nickel nitrosyl and substituted-cyclopentadienyl nickel nitrosyl in which the substituents consist of one to two alkyl radicals of 1 to 2 carbon atoms;

(B) a tetraloweralkyl lead antiknock compound in an amount to provide from about 1 to about 4.23 grams of lead per gallon of said fuel; and

(C) from 0.5 to about 2.5 theories, based on the metals, of at least 1 polyhalohydrocarbon lead scavenger.

14. A motor fuel for spark ignition engines which consists essentially of liquid hydrocarbons boiling in the gasoline range and

(A) a binary mixture of iron and nickel antiknock compounds in an amount to provide a total of from 0.1 to about 1 gram of metal per gallon of said fuel, said binary mixture consisting essentially of

(a) about 85% to about 50% by weight of at least one member of the group consisting of dicyclopentadienyl iron and substituted-dicyclopentadienyl iron in which the substituents consist of one to two alkyl radicals of 1 to 2 carbon atoms, and

(b) about 15% to about 50% by weight of at least one member of the group consisting of cyclopentadienyl nickel nitrosyl and substituted-cyclopentadienyl nickel nitrosyl in which the substituents consist of one to two alkyl radicals of 1 to 2 carbon atoms; and

(B) a tetraalkyl lead antiknock compound in which each alkyl group contains 1 to 2 carbon atoms in an amount to provide from about 1 to about 3 grams of lead per gallon of said fuel; and

(C) from about 1 to about 1.5 theories, based on the metals, of at least 1 polyhaloalkane lead scavenger which consists of 2 carbon atoms, 2–3 halogen atoms of atomic numbers 17–35, and the rest hydrogen atoms.

15. A motor fuel for spark ignition engines which consists essentially of liquid hydrocarbons boiling in the gasoline range and

(A) a binary mixture of iron and nickel antiknock compounds in an amount to provide a total of from 0.1 to about 1 gram of metal per gallon of said fuel, said binary mixture consisting essentially of

(a) about 85% to about 50% by weight of dicyclopentadienyl iron, and

(b) about 15% to about 50% by weight of cyclopentadienyl nickel nitrosyl; and

(B) a tetraalkyl lead antiknock compound in which each alkyl group contains 1 to 2 carbon atoms in an amount to provide from about 1 to about 3 grams of lead per gallon of said fuel; and

(C) from about 1 to about 2.5 theories, based on the metals, of at least 1 polyhaloalkane lead scavenger which consists of 2 carbon atoms, 2–3 halogen atoms of atomic numbers 17–35, and the rest hydrogen atoms.

16. A motor fuel for spark ignition engines which consists essentially of liquid hydrocarbons boiling in the gasoline range and

(A) a binary mixture of iron and nickel antiknock compounds in an amount to provide a total of from about 0.3 to about 0.75 gram of metal per gallon of said fuel, said binary mixture consisting essentially of

(a) about 75% to about 50% by weight of dicyclopentadienyl iron, and

(b) about 25% to about 50% by weight of cyclopentadienyl nickel nitrosyl; and

(B) a tetraalkyl lead antiknock compound in which each alkyl group contains 1 to 2 carbon atoms in an amount to provide from about 1 to about 3 grams of lead per gallon of said fuel; and

(C) about 1 theory, based on the metals, of ethylene dichloride and about 0.5 theory, based on the lead, of ethylene dibromide.

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