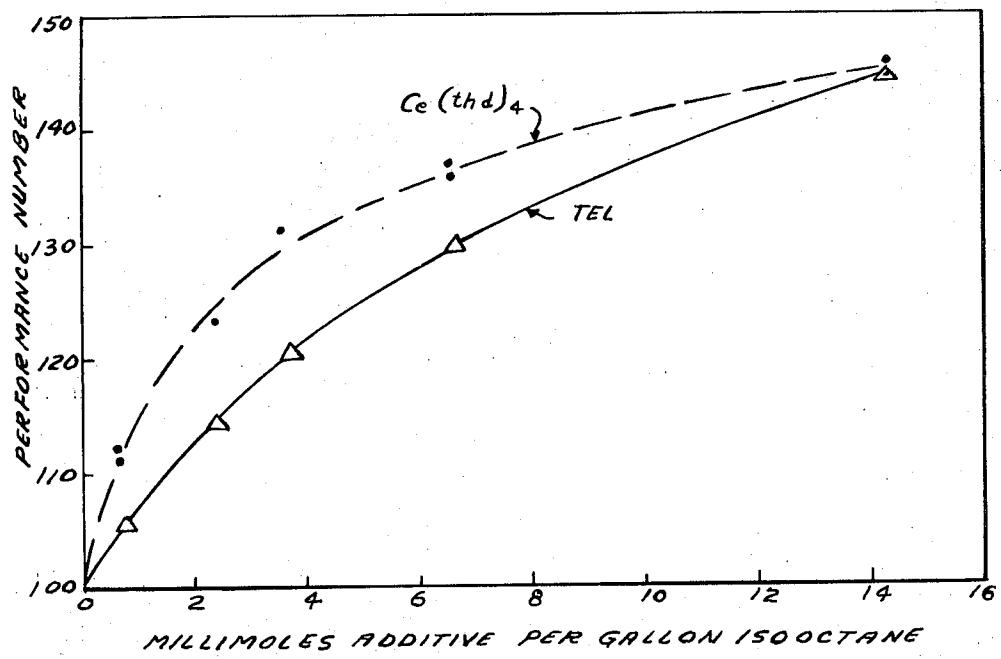


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RARE EARTH BETA-KETOENOLATE ANTI-KNOCK  
ADDITIVES IN GASOLINES  
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RARE EARTH  $\beta$ -KETOENOLATE ANTI-KNOCK ADDITIVES IN GASOLINES

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16 Claims

ABSTRACT OF THE DISCLOSURE

There is disclosed a motor fuel composition which consists essentially of gasoline and, as an antiknock agent, a small amount of a rare earth  $\beta$ -ketoenolate.

FIELD OF THE INVENTION

This invention relates to an improved fuel composition for spark ignition internal combustion engines. In one aspect, the invention relates to a method for improving the antiknock properties of aviation and automotive fuels.

BACKGROUND OF THE INVENTION

The literature is replete with suggestions for improving motor fuels by the addition of a variety of compounds that function as antiknock agents, corrosion inhibitors, carburetor anti-icing agents and pre-ignition inhibitors. Perhaps the greatest amount of effort has been expended in the development of antiknock agents. For example, as disclosed in U.S. Pat. No. 3,003,859, heavy metal derivatives of  $\beta$ -diketones and metallic chelate salts have been proposed as antiknock agents. An earlier patent, namely, U.S. Pat. No. 2,591,503, discloses that various organometallic compounds, including  $\beta$ -diketonate metallic compounds, have been suggested for use as combustion catalysts and refers to several even earlier patents that are concerned with the use of such compounds. It seems that such compounds have not been entirely satisfactory, an important contributing factor to their non-acceptance by industry resulting from their insufficient volatility and stability and their limited solubility in hydrocarbon fuels. Thus, alkyllead compounds, particularly tetraethyllead, continue to be the antiknock agents that are conventionally used.

Because of the requirement to reduce noxious gas emissions from automobile exhausts, car manufacturers may be required to provide their automobiles with converters for decreasing the amount of poisonous gas emissions. As presently planned such converter devices utilize a platinum catalyst. Such a catalyst is very expensive, but an even greater drawback in its use resides in the fact that the catalyst is poisoned by the lead in the alkyllead compound, thereby shortening catalyst life.

It is an object of this invention, therefore, to provide a lead-free antiknock agent which is soluble in hydrocarbon fuels and is at least as effective as alkylleads, such as tetraethyllead.

Another object of the invention is to provide a fuel composition for use in spark ignition internal combustion engines.

A further object of the invention is to provide a fuel composition containing, as the sole antiknock agent, a rare earth  $\beta$ -ketoenolate.

Still another object of the invention is to provide a method for upgrading gasoline so as to obtain automotive and aviation fuels having performance numbers of up to 145.

Other objects and advantages of the invention will become apparent to those skilled in the art upon consideration of the following disclosure and the drawing which is a graph comparing the antiknock effectiveness of tetra-

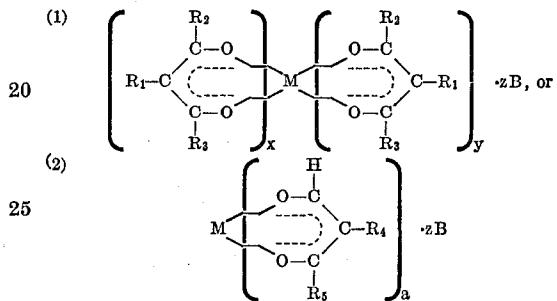
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ethyllead and a preferred antiknock agent of this invention.

SUMMARY OF THE INVENTION

Broadly speaking, the present invention resides in a fuel composition consisting essentially of gasoline and a knock-inhibiting amount of a rare earth  $\beta$ -ketoenolate which is soluble in the gasoline. In another embodiment the invention is concerned with a method for upgrading gasoline to provide a performance number of up to 145 which comprises adding to a petroleum fraction boiling in the gasoline range an antiknock-effective amount of a rare earth  $\beta$ -ketoenolate.

The rare earth  $\beta$ -ketoenolates that are used in the composition of this invention have the following general formulae:



wherein M is a rare earth element selected from the group consisting of lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu), scandium (Sc), yttrium (Y) and mixtures thereof. R<sub>1</sub> is selected from the group consisting of hydrogen, alkyl, phenyl, fluorine, chlorine, bromine and iodine, the alkyl radical preferably containing from 1 to 16 carbon atoms; R<sub>2</sub> and R<sub>3</sub> are individually selected from the group consisting of alkyl, halogen-substituted alkyl, aryl, halogen-substituted aryl, cycloalkyl, hetero atom-substituted alkyl, and hetero atom-substituted aryl; R<sub>1</sub> and R<sub>2</sub> together are d-camphor and R<sub>3</sub> is as indicated; where the total number of carbon atoms in the R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> groups is greater than 3 and the maximum number of carbon atoms in any one of the R<sub>2</sub> and R<sub>3</sub> groups is preferably 35 or less; R<sub>4</sub> is hydrogen or methyl; R<sub>5</sub> is ethyl; B is an adducting agent such as water or a compound containing a donor group; (x+y) equals the valence of the element M or x equals zero and y equals the valence of the element M; a equals the valence of the element M; and z is zero to 5, inclusive.

Specific examples of groups that can be substituted for R<sub>2</sub> and R<sub>3</sub> in Formula 1 include methyl, trifluoromethyl, ethyl, propyl, isopropyl, hepatfluoropropyl, butyl, tertiary butyl, pentyl, heptyl, octyl, dodecyl, hexadecyl, eicosyl, hexacosyl, triacontyl, tritriacontyl, phenyl, biphenyl, phenyl, naphthyl, naphthyl tolyl, p-fluorobenzoyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, triethylamino, tetramethylamino, pyridyl, pyrimidyl, pyrrolyl, pyrrolidyl, thiényl, thenoyl, furoyl, p-methoxyphenyl, and the like.

As indicated above, B in the formulae is water or a compound containing a donor group. The adducting agent can also be defined as a compound having a moiety containing an electron pair capable of bonding to the rare earth element ion. Examples of compounds containing donor groups include ammonia; alcohols, such as methanol, ethanol, isopropanol, and butanol; esters, such as ethyl acetate, n-butyl acetate, ethyl propionate, methyl n-butyrate, ethyl isovalerate, and dimethyl succinate;

amines, such as ethylamine, aniline, diethylamine, ethylphenylamine, triethylamine, methyldiethylamine, tripropylamine, triethanolamine, diphenylbenzylamine, pyridine and piperidine; phosphates, such as tricresylphosphate and tributylphosphate; amides, such as formamide, dimethylformamide, acetamide, ethylacetamide and dibenzamide; ethers, such as ethyl ether, dimethyl ether, methylethyl ether, dimethoxymethane, and dimethoxypropane; sulfoxides, such as dimethylsulfoxide, diethylsulfoxide, dipropylsulfoxide; sulfides, such as dimethylsulfide, diethylsulfide, dibenzylsulfide and diphenylsulfide; ketones, such as acetone, pinacolone, acetylacetone, methyl-4,6-heptanedione, 2-methyl-3,5-octanedione, 2,4-decanedione, and 6,8-tridecanedione; and the like.

The following are examples of rare earth  $\beta$ -ketoenolates that can be used in the practice of the present invention:

tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato) cerium(IV),  
 tris(2,2,6,6-tetramethyl-3,5-heptanedionato)ytterbium(III),  
 tris(2,2,6,6-tetramethyl-3,5-heptanedionato) praseodymium(III),  
 tris(2,2,6,6-tetramethyl-3,5-heptanedionato) neodymium(III),  
 tris(2,2,6,6-tetramethyl-3,5-heptanedionato) lanthanum(III),  
 tetrakis(2,2-dimethyl-3,5-hexanedionato)cerium(IV),  
 tris(2,2-dimethyl-3,5-hexanedionato)praseodymium(III),  
 tris(1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionato)neodymium(III)hydrate,  
 tris(1,1,1-trifluoro-3-methyl-2,4-hexanedionato) samarium(III),  
 tris(1,1,1-trifluoro-3-isopropyl-6-methyl-2,4-heptanedionato)europium(III),  
 tetrakis(1,3-diphenyl-1,3-propanedionato)cerium(IV),  
 tris(1,3-diphenyl-2,4-octanedionato)gadolinium(III),  
 tris(1,1,1-trifluoro-4-phenyl-2,4-butanedionato) terbium(III),  
 tris(1-p-fluorobenzoyl-2,4-butanedionato)dysprosium(III),  
 tris[1,1,1-trifluoro-4(p-biphenyl)-2,4-butanedionato] holmium(III),  
 tris(2-naphthyltrifluoroacetylacetone)erbium(III),  
 tetrakis(1,3-dicyclopropyl-1,3-propanedionato) cerium(IV),  
 tris(1,3-dicyclohexyl)-2,4-butanedionato)cerium(III),  
 tris(2-furyltrifluoroacetylacetone)thulium(III),  
 tris(1-cyclopentyl-1,3-butanedionato)ytterbium(III),  
 tris(tropolonato)scandium(III),  
 tetrakis(2-pyrrolyltrifluoroacetylacetone)cerium(IV),  
 tris(thenoyltrifluoroacetylacetone)lanthanum(III),  
 tris[1,1,1,2,2,3,3-heptafluoro-6(2-thienyl)-4,6-hexanedionato]praseodymium(III),  
 tris(2-pyrryloyltrifluoroacetylacetone)europium(III),  
 bis(2-methyl-4,6-nonanedionato)europium(II),  
 bis(2,6-dimethyl-3,5-heptanedionato)samarium(II),  
 tris(trifluoroacetyl-d-camphorato)europium(III),  
 tris(1,1,1,5,5-hexafluoro-4,6-pentanedionato) dysprosium(III)hydrate,  
 tetrakis(3,5-pentanedionato)cerium(IV),  
 tris(2-methyl-1,3-pentanedionato)lanthanum(III),  
 dimethylformamide adduct of tris(2,2-dimethyl-3,5-hexanedionato)lanthanum(III),  
 triethylamine adduct of tris(1,1,1-trifluoro-3-isopropyl-6-methyl-2,4-heptanedionato)europium(III),  
 butanol adduct of tris(3-methyl-2,4-pentanedionato) praseodymium(III),  
 tricresylphosphate adduct of tris(2-methyl-4,6-heptanedionato)neodymium(III),  
 ethylacetate adduct of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)ytterbium(III),  
 ethyl ether adduct of tris(3-ethyl-2,4-heptanedionato) gadolinium(III),

dimethoxy propane adduct of tris(1,1,1,5,5-hexafluoro-2,4-pentanedionato)erbium(III); and the like.

The  $\beta$ -ketoenolates represented by the above formulae (except for those in which  $R_1$  and  $R_2$  together are d-camphor) and methods for their synthesis are described in the literature. In this regard attention is directed to Inorganic Chemistry, 6, 1105 (1967), Inorganic Chemistry, 10, 498 (1971), Inorganic Synthesis, 11, 94-98 (1968), and Journal of the American Chemical Society, 87, 5254 (1965), which are incorporated herein by reference. The  $\beta$ -ketoenolates in which  $R_1$  and  $R_2$  are d-camphor and  $R_3$  is, for example, a fluoroalkyl, can be synthesized by preparing an alcohol solution of trifluoroacetyl-d-camphor [H(facam)] and adding this solution to an aqueous solution of a chloride of one of the aforementioned rare earth elements. For example, in the synthesis of tris(trifluoroacetyl-d-camphorato)praseodymium(III) [Pr(facam)<sub>3</sub>], a first solution is prepared by stirring 15 millimoles (3.70 grams) of H(facam) in 100 milliliters of a 50 percent alcohol solution. A 10 percent ammonium hydroxide solution is slowly added until all of the H(facam) is dissolved. A second solution is prepared by adding 5 milliliters of a 1 molar aqueous solution of praseodymium chloride (5 millimols) to 30 milliliters of alcohol. The first solution is then added dropwise to the second solution while stirring vigorously. The precipitate that forms is stirred in the mother liquor for an additional time, e.g., for about one hour, after all of the first solution has been added. The mixture is then filtered and the precipitate is washed with 100 milliliters of a 50 percent alcohol solution. After the precipitate is air dried overnight, it is recovered and the product obtained is determined by analysis to be Pr(facam)<sub>3</sub>.

Of the  $\beta$ -ketoenolate derivatives it is preferred to use those in which the rare earth element is cerium. For example, tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)cerium(IV) has been found to be a particularly effective antiknock agent. However, from an economic standpoint, it is often desirable to employ those which are derived from naturally occurring ores so that M in the foregoing formula is a mixture of rare earth elements. Also, it is often preferred to utilize an ore which is rich in cerium. The following table shows the weight percent of oxides of rare earth elements in an ore that is rich in cerium:

	Weight percent
La <sub>2</sub> O <sub>3</sub>	24
CeO <sub>2</sub>	48
Pr <sub>2</sub> O <sub>11</sub>	5
50 Nd <sub>2</sub> O <sub>3</sub>	17
Sm <sub>2</sub> O <sub>3</sub>	3
Gd <sub>2</sub> O <sub>3</sub>	2
Y <sub>2</sub> O <sub>3</sub>	0.2
Other rare earth oxides	0.8
	100.0

It is to be understood that the foregoing is only intended to be exemplary of a rare earth ore and that mixtures of the rare earth elements generally can be used.

60 The rare earth  $\beta$ -ketoenolates are added to a hydrocarbon fuel which is usually used in spark ignition internal combustion engines. Such fuels, which are conventionally classified as automotive or aviation fuels, usually comprise a petroleum fraction boiling in the gasoline hydrocarbon range, e.g., between about 50 and 450° F., and which is comparatively stable as regards gum formation or oxidation. The term "gasoline" as used herein covers such well known fuels which may contain in addition to the anti-knock agent of this invention other materials, such as conventional anti-icing additives, pre-ignition inhibitors, dyes and oxidation inhibitors. The amount of the anti-knock agent that is added generally is in the range of about 0.001 to 50 millimols per gallon of gasoline. While the rare earth  $\beta$ -ketoenolates are generally used as the sole antiknock agent, it is within the scope of the invention.

tion to use them in conjunction with conventional agents, such as lead alkyls, particularly tetraethyllead, and tricresylphosphate. When included in the composition, the amount of the latter compounds that are added is usually in the range of about 0.01 to 2 grams per gallon of gasoline.

A more complete understanding of the invention will be obtained by referring to the following illustrative examples which are not intended, however, to be unduly limitative of the invention.

#### EXAMPLE I

A series of runs was conducted in which the following rare earth  $\beta$ -ketoenolates were added to isoctane:

- (1) tris(2,2,6,6-tetramethyl-3,5-heptanedionato) praseodymium(III) [Pr(thd)<sub>3</sub>],
- (2) tris(2,2,6,6-tetramethyl-3,5-heptanedionato) neodymium(III) [Nd(thd)<sub>3</sub>],
- (3) tris(2,2,6,6-tetramethyl-3,5-heptanedionato) ytterbium(III) [Yb(thd)<sub>3</sub>], and
- (4) tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato) cerium(IV) [Ce(thd)<sub>4</sub>].

The Ce(thd)<sub>4</sub> used in this example was synthesized as described hereinafter. To a 2-liter Pyrex resin vessel containing 0.6 mol of 2,2,6,6-tetramethyl-3,5-heptanedione [H(thd)<sub>4</sub>], there was added 300 milliliters of 95 percent ethanol. The resulting solution was stirred continually during the remainder of the procedure. There was then introduced 0.6 mol of NaOH dissolved in 50 milliliters of distilled water. At this point a clear yellow solution formed, and 0.15 mol of Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O dissolved in 100 milliliters of distilled water was added. A yellow-red precipitate formed. Air was then bubbled through the solution for 2 hours in order to oxidize all of the Ce(III) to Ce(IV). Five hundred milliliters of distilled water was added, and a red-brown precipitate was collected by suction filtration through a medium porosity sintered glass funnel. The precipitate was air dried and then dissolved in boiling methylcyclohexane. The resulting solution was filtered while hot so as to remove any methylcyclohexane insolubles. The material collected on the filter was discarded. The filtrate was cooled and excess solvent was removed by evaporation using an air line. After the solution was cooled to Dry Ice temperature, it was filtered. The pure Ce(thd)<sub>4</sub> red-brown crystals were collected by filtration through a medium porosity sintered glass funnel and air dried. The yield of Ce(thd)<sub>4</sub> was 68 percent, and its melting point was 279–283° C. in a sealed glass capillary. An analysis of the product gave the following percentages; C, 60.76; H, 9.08; O, 13.48 and Ce, 16.68 as compared to theoretical values of C, 60.52; H, 8.77; O, 14.66; and Ce, 16.05.

A run was also carried out in which tetraethyllead (TEL) was added to isoctane. The several fuel compositions were tested to determine their performance and octane numbers. The amounts of the compounds added and the results of the tests are shown below in Table I.

TABLE I

Additive	Grams additive/gal. of isoctane	Mols of metal per gal.	Performance number supercharge method 1	Octane number research method 2
Pr(thd) <sub>3</sub>	0.447	0.00065	106.1	102.03
Nd(thd) <sub>3</sub>	0.451	0.00065	106.1	102.03
Yb(thd) <sub>3</sub>	0.470	0.00065	106.8	102.27
Ce(thd) <sub>4</sub>	0.568	0.00065	111.1	103.70
Tel (calculated)		0.00065	104.9	101.63
Isoctane <sup>3</sup>			100	100

<sup>1</sup> Determined according to method of ASTM D909.

<sup>2</sup> Determined according to method of ASTM D2899.

<sup>3</sup> Contains no additive.

The data in Table I show that Ce(thd)<sub>4</sub> is superior to the other rare earth  $\beta$ -ketoenolates in antiknock effectiveness. Also, Ce(thd)<sub>4</sub> is 431 times more soluble in isoctane than Pr(thd)<sub>3</sub> and even more soluble than the

other rare earth derivatives. Thus, the room temperature solubility of Pr(thd)<sub>3</sub> is 0.12 g./liter of isoctane while that of Ce(thd)<sub>4</sub> is 50.9 g./liter of isoctane. In view of these factors, the cerium compound is the preferred anti-knock agent. However, the data demonstrate that all of the rare earth derivatives gave results superior to those obtainable with tetraethyllead.

#### EXAMPLE II

10 A series of runs was conducted in which Ce(thd)<sub>4</sub> was added to isoctane at various concentration levels. Thereafter, the several fuel compositions were tested to determine their performance numbers. The amounts of the Ce(thd)<sub>4</sub> used and the results of the tests are set forth in Table II.

TABLE II

Ce(thd) <sub>4</sub> , g./gal isoctane	Mol/gal.	Performance number	
		Motor method <sup>1</sup>	Supercharge method <sup>2</sup>
0.568	0.00065	104.0	111.1 <sup>3</sup> (112.2)
2.08	0.00238	107.1	123.1
3.081	0.00353	110.5	131.3
5.73	0.00656	110.5	136.1 <sup>3</sup> (137.0)
12.45	0.01426	115.8	145.0 <sup>3</sup> (145.7)

<sup>1</sup> Determined according to the method of ASTM D2700.

<sup>2</sup> Determined according to the method of ASTM D909.

<sup>3</sup> Fresh compositions prepared and tested with results as indicated in parentheses.

30 A comparison was made of the antiknock effectiveness of TEL and Ce(thd)<sub>4</sub> as a function of molar concentration in isoctane. The results of the comparison are shown below in Table III, and they are depicted graphically in the drawing.

TABLE III

TEL, mol per gal isoctane	Ce(thd) <sub>4</sub> , mol per gal isoctane	Performance number	
		TEL-supercharge method <sup>1</sup>	Ce(thd) <sub>4</sub> supercharge method <sup>2</sup>
0.00065	0.00065	104.9	111.1 <sup>3</sup> (112.2)
0.00238	0.00238	115.0	123.1
0.00353	0.00353	120.0	131.3
0.00656	0.00656	130	136.1 <sup>3</sup> (137.0)
0.01426	0.01426	145	145.0 <sup>3</sup> (145.7)

<sup>1</sup> Theoretical performance numbers as calculated.

<sup>2</sup> Measured performance numbers as shown in Table II.

<sup>3</sup> See footnote 3 of Table II.

45 As seen from the drawing, which graphically represents the data in Table III, at the same concentrations, Ce(thd)<sub>4</sub> is more effective than TEL as an antiknock agent.

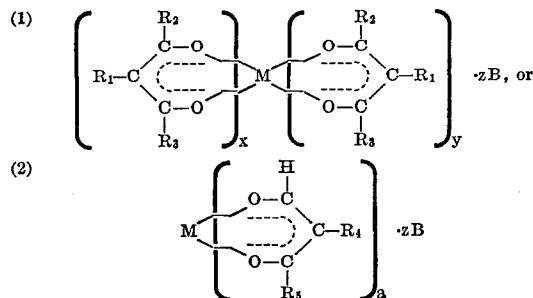
50 From the foregoing examples, it is seen that the present invention provides a lead-free antiknock agent which is capable of furnishing the required performance or octane numbers for fuels used in aviation and automotive engines. The fact that the present antiknock agent is lead-free is particularly significant in view of the fact that lead acts as a poison in catalytic exhaust devices. Thus, the discovery of a replacement antiknock agent for the currently used lead compounds takes on added importance, particularly since there is presently no way to completely eliminate lead from fuels without causing even greater pollution.

55 While the theory as to why the rare earth  $\beta$ -ketoenolates function so effectively as antiknock agents is not completely understood, it is known to be critical that the R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> of the compounds of Formula 1 contain a total of at least 4 carbon atoms. Compounds in which the R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> groups contain less than a total of 4 carbon atoms are much less soluble in hydrocarbon fuels, a factor which renders them ineffective as antiknock agents. Furthermore, the rare earth  $\beta$ -ketoenolates volatilize readily during the combustion process so that they readily alter the combustion process in the vapor state. There are also indications that the combustion products of the antiknock agents function as catalysts to promote oxidation of unburned hydrocarbons, thereby reducing pollutants in the exhaust gases.

In view of the foregoing disclosure, modifications of the present invention can be made by those skilled in the art. Such modifications fall within the spirit and scope of the invention.

We claim:

1. A fuel composition consisting essentially of a gasoline and a knock-inhibiting amount of a  $\beta$ -ketoenolate having the following general formulae:



wherein M is a rare earth element selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, scandium, yttrium, and mixtures thereof; R<sub>1</sub> is selected from the group consisting of hydrogen, alkyl, phenyl, fluorine, chlorine, bromine and iodine; R<sub>2</sub> and R<sub>3</sub> are individually selected from the group consisting of alkyl, halogen-substituted alkyl, aryl, halogen-substituted aryl, cycloalkyl, hetero atom-substituted alkyl and hetero atom-substituted aryl; R<sub>1</sub> and R<sub>2</sub> together are d-camphor and R<sub>3</sub> is as indicated, where the total number of carbon atoms in the R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> groups is greater than 3; R<sub>4</sub> is hydrogen or methyl; R<sub>5</sub> is ethyl; B is water or a compound containing a donor group; (x+y) is equal to the valence of the element M or x equals zero and y is equal to the valence of the element M, a is equal to the valence of the element M; and z is zero to 5, inclusive.

2. The fuel composition of claim 1 in which M is cerium.

3. The fuel composition of claim 1 in which M is praseodymium.

4. The fuel composition of claim 1 in which M is neodymium.

5. The fuel composition of claim 1 in which M is ytterbium.

6. The fuel composition of claim 1 in which M is a mixture of the rare earth elements.

7. The fuel composition of claim 6 in which M is a cerium-rich mixture of the rare earth elements.

8. The fuel composition of claim 1 in which the  $\beta$ -ketoenolate is tetrakis(2,2,6,6 - tetramethyl-3,5-heptanedionato)cerium(IV).

9. The fuel composition of claim 1 in which the  $\beta$ -ketoenolate is tris(2,2,6,6 - tetramethyl-3,5-heptanedionato)praseodymium(III).

10. The fuel composition of claim 1 in which the  $\beta$ -ketoenolate is tris(2,2,6,6 - tetramethyl-3,5-heptanedionato)neodymium(III).

11. The fuel composition of claim 1 in which the  $\beta$ -ketoenolate is tris(2,2,6,6 - tetramethyl-3,5-heptanedionato)ytterbium(III).

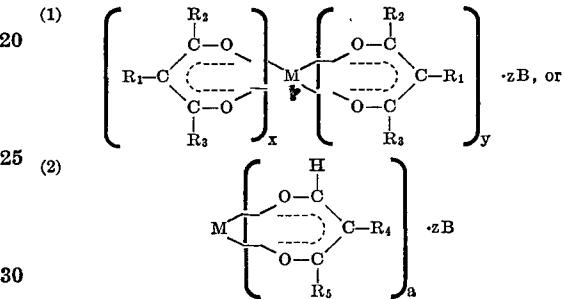
12. The fuel composition of claim 1 in which the  $\beta$ -ketoenolate is tris(2,2,6,6 - tetramethyl-3,5-heptanedionato)cerium(III).

13. The fuel composition of claim 1 in which the amount of  $\beta$ -ketoenolate is in the range of about 0.001 to 50 millimols per gallon of gasoline.

14. The fuel composition of claim 13 which contains 0.01 to 2 grams of an alkyllead or tricresylphosphate per gallon of gasoline.

15. The fuel composition of claim 14 in which the alkyllead is tetraethyllead.

16. In a method of operating an internal combustion in which unburned hydrocarbons are present in the combustion products, the improvement which comprises catalyzing the oxidation of the unburned hydrocarbons by contacting same with a  $\beta$ -ketoenolate having the following general formula:



wherein M is a rare earth element selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, scandium, yttrium, and mixtures thereof; R<sub>1</sub> is selected from the group consisting of hydrogen, alkyl, phenyl, fluorine, chlorine, bromine and iodine; R<sub>2</sub> and R<sub>3</sub> are individually selected from the group consisting of alkyl, halogen-substituted alkyl, aryl, halogen-substituted aryl, cycloalkyl, hetero atom-substituted alkyl and hetero atom-substituted aryl; R<sub>1</sub> and R<sub>2</sub> together are d-camphor and R<sub>3</sub> is as indicated, where the total number of carbon atoms in the R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> groups is greater than 3; R<sub>4</sub> is hydrogen or methyl; R<sub>5</sub> is ethyl; B is water or a compound containing a donor group; (x+y) is equal to the valence of the element M or x equals zero and y is equal to the valence of the element M, a is equal to the valence of the element M; and z is zero to 5, inclusive.

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U.S. Cl. X.R.

44-68; 252-386

**Notice of Adverse Decision in Interference**

In Interference No. 98,778, involving Patent No. 3,794,473, K. J. Eisentraut, R. L. Tischer and R. E. Sievers, RARE EARTH  $\beta$ -KETOENOLATE ANTI-KNOCK ADDITIVES IN GASOLINES, final judgment adverse to the patentees was rendered Aug. 17, 1976, as to claims 2, 8, 13 and 16.

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