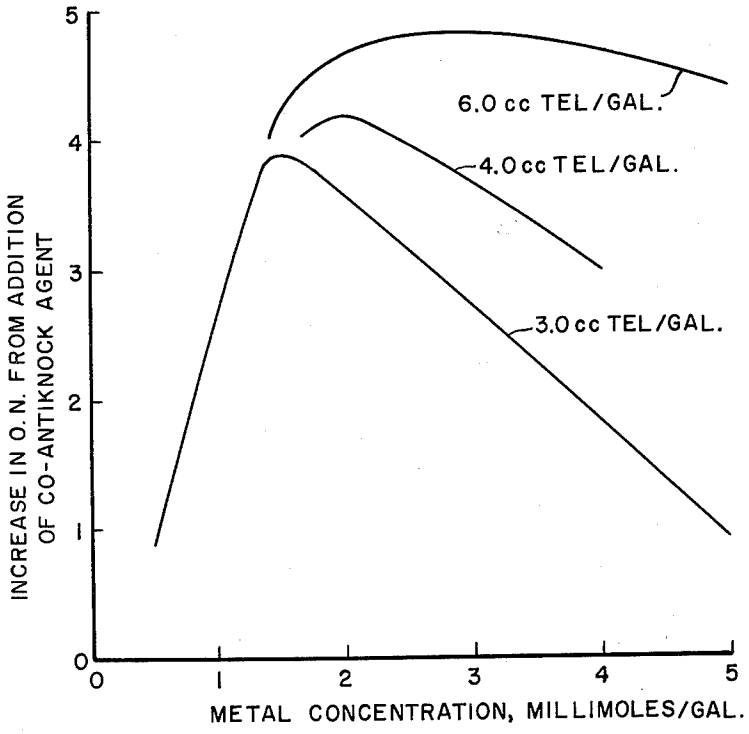
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GASOLINE COMPOSITION

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GASOLINE COMPOSITION

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This invention relates to improved hydrocarbon fuel compositions and particularly to improved motor gasoline fuel compositions having high octane numbers.

Recent automotive design trends have been toward engines having greater power for the same size engine and more efficient utilization of the gasoline fuel. Engine designers have accomplished this largely by steadily raising the compression ratios of automotive engines, which has necessitated the use of fuels having increased resistance to detonation or spark knock. There is also an increased demand for aviation fuels having greater anti-knock properties. It has heretofore been possible to manufacture such fuels from crude petroleum by the development and utilization of new hydrocarbon conversion and synthesis processes such as cracking, reforming, polymerization, and alkylation. The resistance to knock of the fuels from these processes is even further augmented by the addition of antiknock agents such as tetraethyllead (TEL), and, recently, methylcyclopentadienyl manganese tricarbonyl. Resistance to spark knock is, of course, evaluated as "octane number." Therefore, the demand for fuels having greater resistance to spark knock is manifested in the constantly increasing octane number of premium fuels. However, as the octane number of modern gasoline fuels has been raised, there has been a concomitant decrease in the susceptibility of such fuels to octane number improvement by addition of organo-metallic antiknock agents. It becomes less economical, therefore, to obtain greater resistance to spark knock by this means with higher octane number fuels. In addition, the amount of organo-metallic additive which is added to motor fuels may also be limited by consideration of the degree of toxicity imparted to the fuel containing such materials. For this reason, the maximum amount of tetraethyllead which may be added to commercial gasoline motor fuels is 3 or 4 cc./gal. (US) and 6 cc./gal. (US) for automotive and aviation fuels, respectively. Consequently, the degree of octane number improvement which can be obtained in this manner is limited. Organo-metallic antiknock additives are difficult to synthesize and are expensive. Their addition to fuels is thus limited to small concentrations by considerations of economics as well. Yet another limitation on the use of such antiknock additive-containing fuels is the tendency of the antiknock additives therein to lay down large quantities of deposits in the combustion chamber of the engine, which may contribute to an increase in the octane number requirement of the engine. Because of these limiting factors on the use of conventional organo-metallic antiknock additives, the octane number obtainable from gasoline fuels made by conventional refining processes has also been limited.

There have been many attempts to solve this problem by the use of two or more antiknock agents. However, in most of these situations, the incremental increase in octane number obtained by adding the second antiknock agent has been considerably less than the octane number increase obtainable when the supplemental antiknock agent is added to the gasoline by itself. That is, the antiknock activity of the supplemental antiknock agent or of both antiknock agents is less, on the basis of the volume added, than either by itself. Consequently, even though significant increases in octane number are obtainable, it has heretofore been uneconomical to obtain higher octane number motor gasoline in this manner.

It is therefore an object of this invention to provide improved gasoline fuel compositions. It is also an object of the invention to augment the efficacy of tetraethyllead as an antiknock additive in gasoline. It is a further object of the invention to provide higher detonation resistance in gasoline in an economical manner. It is still another object to provide hydrocarbon compositions which enhance the efficiency of antiknock additives added thereto. Another object is to attain the foregoing objects without detrimental side effects in the use of the fuel in gasoline engines. A still further object of the invention is to provide an improved antiknock additive concentrate composition.

The attainment of these and other objects will be apparent from the detailed description of the invention which is a gasoline motor fuel composition containing a tetraalkyllead compound as a primary antiknock agent and small but critical amounts of certain organo-metallic compounds which by themselves exhibit no primary antiknock activity, and from the drawing, consisting of a single figure, which illustrates graphically the effect of the antiknock agent upon the octane number of gasoline containing various quantities of tetraethyllead.

The use of organo-metallic compounds as primary antiknock agents has long been known, and countless numbers of these materials have been suggested, tried, and used with various degrees of success. The most widely used for many reasons, including availability, economy, and antiknock activity, are the tetraalkylleads, particularly tetraethyllead. However, it has now been found that certain organo-metallic compounds, which possess essentially no primary antiknock activity when they are added to gasoline containing no other antiknock agent, nevertheless when added to leaded gasolines of selected composition as to hydrocarbon type and boiling range, possess extraordinary co-antiknock activity. By co-antiknock activity, it is here meant that the secondary or co-antiknock agent causes the octane number of the gasoline containing both primary and secondary antiknock additives to be raised significantly above the level which is obtained by the primary antiknock agent alone, the co-antiknock effect being the result of co-action of the secondary with the primary additive rather than any primary antiknock properties of the secondary additive alone.

The addition of very small amounts of organo-metallic compounds corresponding to the structural formula

$$(Z-A\overset{Y}{\nearrow}Y)_mM$$

to fuels containing tetraalkyllead primary antiknock agents has been found to raise the octane number of the total mixture by as much as 4.5 octane numbers or even more.

In the foregoing structural formula

$$(Z-A\overset{Y}{\nearrow}Y)_mM$$

M is a metal selected from the group consisting of antimony, bismuth, cobalt, copper, nickel and tellurium, A is selected from the group consisting of carbon and phosphorus, and Z is selected from the group consisting of $(RY)_2$ when A is phosphorus and (R_nX) when A is carbon. The symbol Y denotes a chalcogen atom having an atomic number of from 8 to 16, inclusively, X is selected from the group consisting of nitrogen and chalcogen having an atomic number of from 8 to 16, inclusively, and R is a monovalent hydrocarbyl group containing from 3 to 15 carbon atoms per molecule. The symbol *n* denotes a whole number of from 1 to 2 which

is one less than the valence of X, and *m* is a whole number corresponding to the valence of M.

The enhancement of octane number quality afforded by the addition of extremely small quantities of organic metallic compounds corresponding to the foregoing formula may be observed by reference to the following example.

EXAMPLE I

A number of compounds corresponding to the formula

$$(Z-A\overset{Y}{\nearrow}Y)_mM$$

were each added in the same concentration to separate samples of a commercial light olefin isobutane alkylate containing 3 cc. tetraethyllead (TEL) per US gallon. The octane number of all the samples containing secondary additive and also a separate sample of the same alkylate containing only 3 cc. TEL/gal. (US) were determined by the Research Method. (ASTM test designation D-357-53). To determine the increase in octane number obtained by adding small amounts of co-antiknock agent, the difference in the octane numbers of the samples with and without co-antiknock agent (Δ O.N.) were calculated. The results are tabulated below.

TABLE I

Secondary antiknock agent, composition	Concentration, millimoles/gallon (US)	Octane number, enhancement
Copper dibutyldithiocarbamate	1.6	4.3
Nickel dibutyldithiocarbamate	1.6	3.8
Cobalt dibutyldithiocarbamate	1.6	2.2
Manganese dibutyldithiocarbamate	1.2	0.0
Antimony diamyldithiocarbamate	1.4	1.0
Lead diamyldithiocarbamate	2.0	−0.5
Zinc diamyldithiocarbamate	1.6	−0.1
Cadmium diamyldithiocarbamate	1.5	−0.5
Copper diamyldithiocarbamate	1.6	3.9
Tellurium diamyldithiocarbamate	5.0	2.0
Bismuth diamyldithiocarbamate	5.6	1.0
Copper 0,0-dilaurylthionothiophosphate	2.0	3.4

Only metals from periodic groups I, V, VI and VIII have been found to be effective. The members of groups I and VIII having atomic numbers of from 27 to 29, inclusively, have been found to be particularly effective and are therefore the preferred metallic constituents (M) of the co-antiknock agent in accordance with the invention. Copper is particularly preferred.

Composition of the hydrocarbyl group R in the foregoing formula for the co-antiknock agents of the invention is important even though a wide range of compositions may be used. It has been found that R must contain at least 3 carbon atoms per molecule, but may contain as many as 15 carbon atoms per molecule. The configuration of R is, however, not narrowly critical. Thus, R may be alkyl, aryl, arylalkyl, alkylaryl, alkenyl, or cycloalkenyl.

The R group may also be substituted with, for example, halogen atoms and oxygen-containing groups such as hydroxyl, epoxy, and keto oxygen atoms. However, such substitutions must be limited to the extent that the hydrocarbon solubility of the compound is not substantially reduced. It is preferred that the co-antiknock agents be completely soluble in gasoline hydrocarbons. In any event, the solubility of the co-antiknock agent must not be less than about 80% by volume, below which the co-antiknock action of the compounds is likely to be considerably reduced because of maldistribution to the cylinders of the engine.

When A is carbon, X is nitrogen, and Y is sulfur, i.e., when the compound is a dithiocarbamate, it is particularly preferred that the two Rs are both alkyl groups with from 4 to 8 carbon atoms.

The data in the foregoing table, of course, show that large increases in octane number are obtainable at ex-

tremely low metal concentrations. In view of the fact that the increases obtained were of the same magnitude as that obtained with many primary antiknock materials at much higher concentrations, for example, 15 to 30 millimoles per gallon, it is apparent that the organo-metallic secondary anti-detonant materials are not acting in the manner of a primary antiknock agent. That is, the secondary antiknock additives are acting in conjunction with or co-acting with the tetraethyllead. As confirmation of this, the following tests were performed.

EXAMPLE II

Several metal dialkyldithiocarbamates were each added in amounts varying from 1 to 10 millimoles of copper per gallon (US) of fuel to each of several samples of a commercial alkylate containing 3 cc. TEL/gallon (US). The Research Octane number of each sample containing the metallic co-antiknock agent and also a sample containing only TEL and no co-antiknock compound were then obtained. By subtracting the octane number of the blend containing no co-antiknock agent from the octane number of the blends containing co-antiknock agent, a measure of the octane number enhancement (Δ O.N.) at various ratios of metal-to-lead was obtained. The results were as follows:

TABLE II

Copper Diamyldithiocarbamate

Concentration of metal dialkyldithiocarbamate			Δ O.N.
Gm. metal/gm. Pb	Millimoles metal/millimole Pb	Millimoles metal/gal. (US)	
0.010	0.034	0.5	0.9
0.021	0.069	1.0	2.5
0.032	0.103	1.5	3.9
0.053	0.172	2.5	3.0
0.105	0.344	5.0	1.2

Copper Dioctyldithiocarbamate

0.021	0.069	1.0	1.2
0.032	0.103	1.5	1.8
0.053	0.172	2.5	3.2
0.105	0.344	5.0	2.9
0.211	0.688	10.0	1.8

Nickel Dioctyldithiocarbamate

0.020	0.069	1.0	0.4
0.029	0.103	1.5	1.0
0.049	0.172	2.5	2.3
0.098	0.344	5.0	2.3
0.195	0.688	10.0	0.4

Cobalt Dioctyldithiocarbamate

0.020	0.069	1.0	1.1
0.029	0.103	1.5	2.0
0.049	0.172	2.5	2.0
0.098	0.344	5.0	2.6
0.196	0.688	10.0	1.1

The above data show that the co-action of the secondary or co-antiknock additives is present only at small concentrations. In addition, it may also be seen that the greatest benefit is obtained at very low metal ratios. (Metal ratio as used in the context of this specification refers to the weight ratio of metal in the secondary or co-antiknock agent to the lead in the tetraalkyllead when both are added to gasoline compositions in accordance with the invention.)

The data in Table II also show that the secondary antiknock agents are effective in concentrations ranging from as little as 0.5 milimole per gallon to as high as 10 millimoles per gallon. Even higher concentrations can, of course, be used. However, it is apparent from these data that the octane number enhancement is reduced thereby. Even the optimum concentration varies considerably with

the particular co-antiknock material which is used. The greatest octane number benefits obtained by the co-antiknock agent in gasoline containing 3 cc. TEL per gallon are at concentrations of from about 1.0 to about 5.0 millimoles of metal contained in the co-antiknock agent per gallon of fuel.

Though most commercial gasoline type fuels contain lead, usually at tetraethyllead, the amount varies widely. Generally, in the case of automotive fuels, the composition will contain at least about 0.5 cc. TEL/gallon and not more than about 4.0 cc. TEL/gallon, which is the maximum permissible concentration in the United States because of the extreme toxicity of TEL. In the case of avaiation fuels, however, even higher TEL concentrations are used, e.g., as high as 6.0 cc. TEL/gallon of fuel. Therefore, in order to determine the effect of lead concentration on the co-antiknock activity of the foregoing discussed co-antiknock agents, the following test was performed.

EXAMPLE III

A number of duplicate samples of commercial butene-isobutane alkylate were prepared which contained amounts of tetraethyllead varying from 3 to 6 cc. TEL/gallon. One of each duplicate sample was then divided into at least four smaller samples to each of which was added from 0.5 to 5 millimoles/gallon of copper diamyldithiocarbamate. The Research octane numbers of all the samples were then determined. By subtracting the octane numbers of the samples containing only TEL from the octane number of the samples containing co-antiknock agent and TEL (at the same concentration), a measure of octane number enhancement (Δ R.O.N.) due to the presence of the co-antiknock agent was obtained which was then correlated as a function of both co-antiknock concentration and TEL concentration.

The results, which are shown graphically in the drawing, show that the optimum concentration of co-antiknock metal, in millimoles per gallon, is about 1.5, 2.0 and 3 for the fuels containing 3, 4 and 6 cc. TEL/gallon, respectively. Since the optimum co-antiknock concentration is essentially directly proportional to the primary anti-knock concentration, it is apparent that the metal ratio of the two additives (as defined hereinbefore) is critical and is definitive of the operable range of co-antiknock concentrations. Though metal ratios of as high as 0.2 and even higher at large lead concentrations could be used, the preferred range of metal ratio is from about 0.01 to about 0.10. A metal ratio of from about 0.02 to about 0.065 is particularly preferred. Though the foregoing examples have employed only up to 6.0 cc. TEL/gallon, the fuel compositions in accordance with the invention may contain even greater amounts of tetraethyllead, e.g., 12 cc. TEL/gallon and higher.

Though the co-antiknock agents used in accordance with the invention are very effective in isoparaffinic fuels, their use is not limited thereto. However, the composition of the hydrocarbon fuel as to boiling range and especially hydrocarbon type exert a profound effect on the activity of co-antiknock compounds, which may be observed in the following example.

EXAMPLE IV

A large number of refinery hydrocarbon products were blended to different concentrations with motor gasoline alkylate, which consisted of 100% by volume isoparaffins from the alkylation of butenes with isobutane. Duplicate samples of each blend were obtained and tetraethyllead was added to a concentration of 3 cc. TEL/gallon of blend. Additionally, copper diamyldithiocarbamate was added to one of each duplicate samples until the concentration of co-antiknock agent was 1.6 millimoles per gallon of blend. The Research octane numbers of each set of samples were then obtained and the difference between the octane numbers of the samples with and without the secondary antiknock additive (Δ R.O.N.) were noted. The results are given in the following tabulation.

TABLE III

Hydrocarbon blending component				Alkylate, amount in total blend (percent vol.)	Co-antiknock agent	
Principal hydrocarbon type	Composition	Boiling range (° F.)	Amount in total blend (percent vol.)		Concentration (mmoles/gal.)	Increase in research O.N. on adding co-antiknock agent (Δ R.O.N.)
				100	1.6	3.6
Saturates	70% isopentane, 30% of—					
	n-Butane	31–82	19.5	80.5	1.6	2.3
	n-Heptane	208	2.5	97.5	1.6	1.6
	Do	208	10.0	90.0	1.6	1.1
	Mixed iso- and n-paraffins	130–230	15.0	85.0	1.6	1.8
Olefins	Diisobutylene	215	5	95	1.6	4.3
	Do	215	10	90	1.6	4.9
	Do	215	15	85	1.6	3.7
	Do	215	20	80	1.6	2.2
	Do	232	10	90	1.6	4.5
Aromatics	Toluene	232	20	80	1.6	2.0
	Do	80–400	31	69	1.6	1.0
	Thermally reformed catalytic reformate (55% aromatics)	385–470	10	90	1.6	1.2
	Alkyl benzenes	385–470	10	90	1.6	1.2
	Alkyl naphthalenes	410–470+	10	90	1.6	0.3
	Catalytic reformate	380	1	99	1.6	2.6
	Tetrahydronaphthalene	380	2	98	1.6	0.0
	Do	400	1	99	1.6	0.0
	Diamylnaphthalene					

Effect of Iso and Normal Paraffins on Co-Antiknock Activity

The addition of light isoparaffins, i.e., those having less than 8 carbon atoms per molecule, is beneficial to the action of the co-antiknock agent. However, the addition of heavier isoparaffins reduces the co-antiknock effect considerably. It is therefore preferred that the gasoline compositions in accordance with the invention not contain greater than about 20% by volume of isoparaffins boiling over about 300° F. It is even further preferred that the gasoline composition contain no more than about 10% by volume of isoparaffins boiling above about 300° F.

Because of the detrimental effect of normal paraffins in reducing the octane number, the gasoline compositions in accordance with the invention preferably contain essentially no normal paraffins having 7 or more atoms per molecule and only small amounts, preferably not over 10%, of normal paraffins having 5 or 6 carbon atoms per molecule. Fuel compositions containing essentially

no normal paraffins having 5 or more carbon atoms per molecule are particularly preferred. Normal paraffins having less than 5 carbon atoms per molecule, for example, normal butane, having high octane numbers, are useful to provide the gasoline with proper vapor pressure and are not deleterious to the action of the co-antiknock agents.

Effect of Cycloparaffins (Naphthenes)

The gasoline compositions of the invention should contain no more than 10% by volume naphthenes boiling above about 300° F., and preferably substantially none, because they are delterious both with regard to blending octane number and their effect on the response of the co-antiknock agent. There is no limit, however, in the broad aspects of the invention, to the maximum concentration of naphthenes boiling below about 300° F.

Effect of Olefins on Co-Antiknock Activity

The incorporation of up to about 10% of lighter olefins, especially those which are branched, is actually beneficial to the co-action of the co-antiknock agents with tetraethyllead. Moreover, the gasoline compositions of the invention can advantageously contain up to 30% by volume olefins, but larger quantities are deleterious and should be avoided.

Effect of Aromatics

Aromatics boiling below about 300° F., i.e., C_8 aromatic hydrocarbons and lighter, have been found to be not greatly delterious in minor concentrations, e.g., below about 50% by volume. Heavier aromatics, however, which boil above 300° F. are delterious and should not exceed about 20% by volume of the total gasoline blend. In fact, in order to obtain more practical benefits from the co-antiknock agent, it is preferred that the gasoline of the invention contain no more than about 10% by volume of aromatics boiling above 300° F., and no more than 30% by volume of total aromatics.

Though the delterious effect of high boiling aromatics on the effectiveness of the co-antiknock additives is quite unfortunate, it has been found that a very surprising relationship exits between the effect of heavy aromatics and the presence of light naphthenes. That is, light naphthenes suppress the deleterious effects of heavy aromatics. In accordance with applicants' copending patent application Serial No. 18,255, it is possible to have substantial amounts of aromatics boiling above 300° F. in a base gasoline and still obtain large benefits from co-antiknock additives, as long as light naphthenes, i.e., naphthenes boiling below about 300° F., are also incorporated in the base gasoline.

In general, it appears that one volume percent of light naphthenes can overcome completely the deleterious effect of one volume percent of heavy aromatics. However, since practical benefits are obtained up to 10% and 20% by volume heavy aromatics even in the absence of naphthenes, it is not necessary always to have present as much light naphthenes as would be needed to completely cancel the effect of the heavy aromatics. The light naphthenes can be used to obtain even greater benefits from the co-antiknock additives in gasolines which must contain aromatics boiling above 300° F. to have proper volatility distribution of high octane number components. To take advantage of light naphthenes in accordance with this preferred aspect of the invention, it is desirable that the base gasoline contain at least ¼% by volume, or preferably at least ½% by volume, of naphthenes boiling below 300° F. for each 1% by volume of aromatics boiling above 300° F. in excess of 10% by volume of such aromatics, and preferably such amounts of light naphthenes for each 1% by volume of all of such aromatics.

The adverse effect of each of the deleterious or antagonistic components, that is, aromatics, olefins, C_5 plus normal paraffins and heavy naphthenes, is not however, independent. Even with the use of naphthenes in accordance with above, the presence of two or more of such antagonists in maximum concentrations can result in a fuel having little or no response to the action of the co-antiknock agents. Such non-responsive hydrocarbon compositions may be avoided, however, if the compositions meet the following empirical correlation which constitutes a limitation on the total equivalent amount of co-antiknock antagonists (A_E) which may be present in the hydrocarbon blend.

$$A_E = A_L + 1.3A_H + 0.7A_O + 0.25A_P \leqq 50 + 0.75N$$

wherein

A_L=percent by volume of aromatics boiling below 300° F.

A_H=percent by volume of aromatics boiling above 300° F.

A_O=percent by volume of olefins.

A_P=percent by volume of C_5 plus normal paraffins and naphthenes boiling above 300° F.

N =percent by volume of naphthenes boiling below 300° F.

Summing up its broad aspects, the invention therefore resides in the discovery that compounds having the formula

$$(Z{-}A{-}\overset{Y}{\nearrow})_m M$$

as defined hereinbefore, are effective as co-antiknock agents with tetraethyllead when both are added to gasoline blends containing essentially no normal paraffins containing 7 or more carbon atoms, no more than 10% by volume of C_5 to C_6 normal paraffins, no more than 20% by volume of isoparaffins boiling above 300° F., no more than 10% by volume of naphthenes boiling above 300° F., no more than 30% by volume olefins, no more than 50% by volume of total aromatics and no more than 20% by volume of aromatics boiling above 300° F., the composition of the gasoline blends being within the limits defined by the empirical relationship

$$A_E = A_L + 1.3A_H + 0.7A_O + 0.25A_P \leqq 50 + 0.75N$$

Of the members of the class of co-antiknock compounds which are the subject of this invention, the dialkyldithiocarbamates and dialkylthionothiophosphates are preferred. Dialkyldithiocarbamates having from 4 to 8 carbon atoms in each of the alkyl groups are particularly preferred.

In the foregoing examples in which TEL was used as primary antidetonant, the TEL was added in the form of the commercial motor mix, which has the following approximate composition.

Component:	Percent by weight
Tetraethyllead	61.48
Ethylene dibromide (0.5 theory)	17.86
Ethylene dichloride (1.0 theory)	18.81
Dye	0.06
Kerosene and impurities	1.79

The co-antiknock materials of the invention are, however, equally effective in leaded gasoline containing pure TEL with no halohydrocarbon scavenger, or in leaded gasoline containing TEL with ethylene dibromide (e.g., 1.0 theory) and no ethylene dichloride.

Besides the aforementioned halogen-containing lead scavengers, the fuel compositions of the invention can, and ordinarily will, contain other additives, for example, dyes, spark plug antifoulants such as tricresyl phosphate, dimethyl xylyl phosphate, and diphenyl cresyl phosphate, combustion modifiers such as alkyl boronic acids and lower alkyl phosphates and phosphites, oxidation inhibitors such as N,N'-disalicylal-1,2-propanediamine, and rust inhibitors such as polymerized linoleic acids and N,C-disubstituted imidazolines, and the like.

It is to be understood that the order of mixing the various constituents of the compositions of the invention

is immaterial. For example, the co-antiknock compound may be added to a gasoline which already contains the tetraethyllead primary antiknock material. Likewise, the co-antiknock and primary antiknock compounds may be first mixed, stored, and handled as a concentrate, and added to the gasoline at a later time. A gasoline additive concentrate of this latter type may also contain halogen scavenger and spark plug antifouling compound. Under other circumstances, it may be desirable to mix the halogen scavenger and the primary antiknock compound, or the primary antiknock and co-antiknock compounds, in the desired relative proportions and handle or store this mixture, with or without stabilizers, antifouling compounds, inhibitors, etc., as a concentrate for incorporation with the other components of the ultimate fuel composition.

When an additive concentrate of this latter type is employed, it is preferred that it contain an optimum or near optimum metal ratio. Such a concentrate will therefore contain from 0.01 to 0.10 gram of metal in the co-antiknock agent per gram of lead in the tetraethyllead. Preferably, such a concentrate contains from about 0.02 to about 0.065 gram of metal per gram of lead.

A typical additive concentrate in accordance with the invention and containing both TEL motor mix and phosphorus compound for ignition control as well as co-antiknock agent has the following composition:

Component:	Percent by weight
Tetraethyllead	49.0–58.9
Ethylene dibromide	14.2–17.1
Ethylene dichloride	15.0–18.1
Phosphorus (as tricresyl phosphate)	3.8–12.5
Copper (as copper diamyldithiocarbamate)	0.4–7.9
Kerosene, dye, impurities	1.4–1.7

We claim as our invention:

1. A motor gasoline fuel composition consisting essentially of a mixture of hydrocarbons having an ASTM boiling range below about 400° F., an octane number-improving amount of tetraethyllead, and a co-antiknock agent having the structural formula



wherein M is a metal selected from the group consisting of antimony, bismuth, cobalt, copper, nickel, and tellurium, Y is a chalcogen atom having an atomic number of from 8 to 16, inclusively, A is selected from the group consisting of carbon and phosphorus, Z is selected from the group consisting of $(RY)_2$ when A is phosphorus and (R_nX) when A is carbon, X is selected from the group consisting of nitrogen and chalcogen having an atomic number of from 8 to 16, inclusively, R is a monovalent hydrocarbyl radical containing from 3 to 15 carbon atoms per molecule, n is a whole number of from 1 to 2 which is one less than the valence of X, and m is a whole number corresponding to the valence of the metal M, the amount of co-antiknock agent corresponding to from about 0.01 to about 0.10 gram of metal contained in the co-antiknock agent per gram of lead contained in the tetraethyllead, said mixture of hydrocarbons being comprised of (1) no more than 50% by volume aromatics, (2) no more than about 30% by volume olefins, (3) no more than about 20% by volume each of isoparaffins and aromatics boiling above about 300° F., (4) no more than about 10% by volume each of normal paraffins having 5 to 6 carbon atoms per molecule and naphthenes boiling above about 300° F., and (5) essentially no normal paraffins having greater than 6 carbon atoms per molecule, and further characterized as having an equivalent amount of co-antiknock antagonists (A_E) not exceeding $50+0.75N$ wherein A_E and N are defined as hereinbefore in the specification.

2. The fuel composition of claim 1 which is comprised of (1) no more than about 30% by volume of aromatics, (2) no more than about 20% by volume each of olefins and aromatics boiling above about 300° F., (3) no more than about 10% by volume each of isoparaffins boiling above about 300° F. and naphthenes boiling above about 300° F., and (4) essentially no normal paraffins having greater than 4 carbon atoms per molecule, and further characterized as having an equivalent amount of co-antiknock antagonists (A_E) not exceeding $50+0.75N$ wherein A_E and N are defined as hereinbefore in the specification.

3. The motor gasoline fuel composition of claim 1 in which M is a metal having an atomic number of from 27 to 29, inclusively.

4. The motor gasoline fuel composition of claim 1 in which M is copper.

5. The motor gasoline fuel composition of claim 1 in which the co-antiknock agent is a metal dialkyldithiocarbamate in which the alkyl groups each contain from 4 to 8 carbon atoms.

6. The motor gasoline fuel composition of claim 5 in which the co-antiknock agent is copper dialkyldithiocarbamate.

7. The motor gasoline fuel composition of claim 5 in which the co-antiknock agent is nickel dialkyldithiocarbamate.

8. The motor gasoline fuel composition of claim 5 in which the co-antiknock agent is cobalt dialkyldithiocarbamate.

9. The motor gasoline fuel composition of claim 5 in which the co-antiknock agent is antimony dialkyldithiocarbamate.

10. The motor gasoline fuel composition of claim 5 in which the co-antiknock agent is copper dialkyldithiocarbamate.

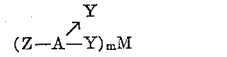
11. The motor gasoline fuel composition of claim 5 in which the co-antiknock agent is tellurium dialkyldithiocarbamate.

12. The motor gasoline fuel composition of claim 5 in which the co-antiknock agent is bismuth dialkyldithiocarbamate.

13. The motor gasoline fuel composition of claim 1 in which the co-antiknock agent is a metal 0,0-dialkylthionothiophosphate.

14. The motor gasoline fuel composition of claim 13 in which the co-antiknock agent is copper 0,0-dilauryl-thionothiophosphate.

15. A gasoline additive concentration composition consisting essentially of a mixture of tetraethyllead and a co-antiknock agent having the structural formula



wherein M is a metal selected from the group consisting of antimony, bismuth, cobalt, copper, nickel, and tellurium, Y is a chalcogen atom having an atomic number of from 8 to 16, inclusively, A is selected from the group consisting of carbon and phosphorus, Z is selected from the group consisting of $(RY)_2$ when A is phosphorus and (R_nX) when A is carbon, X is selected from the group consisting of nitrogen and chalcogen having an atomic number of from 8 to 16, inclusively, R is a monovalent hydrocarbyl radical containing from 3 to 15 carbon atoms per molecule, n is a whole number of from 1 to 2 which is one less than the valence of X, and m is a whole number corresponding to the valence of the metal M, the amount of co-antiknock agent corresponding to from about 0.01 to about 0.10 gram of metal contained in the co-antiknock agent per gram of lead contained in the tetraethyllead.

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