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GASOLINE FUELS

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This invention relates to the improvement of organolead material and in particular to adjuvants for tetraethyllead and tetraethyllead-containing compositions.

Organolead compounds have long been known as antiknock agents for fuel adapted for use in spark ignition type internal combustion engines. Thus, it has been proposed in the prior art to use lead aryls such as tetraphenyllead and lead alkyls such as tetramethyllead, tetraethyllead, tetrapropyllead, dimethyldiethyllead, and the like as antiknock agents. Of these materials, however, only tetraethyllead has attained commercial success because of its efficacious attributes. Likewise, it has long been known that the effective utilization of such antiknock agents is enhanced by using materials known in the art as scavengers. Such materials are generally organic bromine and/or chlorine compounds, ethylene dibromide and ethylene dichloride serving as examples. In order to simplify blending operations, combinations of an organolead antiknock agent and scavengers, termed antiknock fluids, have been provided. In addition to the aforesaid components it has been common practice to employ in commercially available antiknock fluids additional substances such as dyes and blending agents. For example, it has been found that the use of organic dyestuffs in antiknock fluids greatly facilitates fuel blending in that the color of the fluid serves as an indication of its composition.

Organolead compounds, however, suffer one disadvantage, particularly during storage, handling and blending operations, to wit, such compounds are inherently unstable, Thus, organolead compounds in general, and tetraethyllead in particular, are susceptible of deterioration which is largely dependent upon the nature of the environment. By way of example, it has been found that organolead antiknock agents and antiknock fluids containing the same when in contact with certain metals such as copper and copper-containing alloys tend to deteriorate even in a reducing atmosphere. Such deterioration is postulated to result from an adverse catalytic activity exhibited by such metals. In other words, it is generally believed that copper and like metals act as self-perpetuating decomposition accelerators. Another condition enhancing the deterioration of organolead antiknock agents is contact with air. It is generally believed that atmospheric constituents, notably oxygen and ozone, tend to oxidize one or more of the lead-to-carbon bonds with the formation of insoluble decomposition products. Under these conditions there contemporaneously occurs a color change in the dyestuff normally present in antiknock fluids such that the visual identification of the product frequently becomes difficult if not impossible. Organolead antiknock agents are likewise decomposed on exposure to strong light particularly sunlight. In this case, the decomposition is attributed to the catalytic decomposition of the organolead compounds by ultraviolet light. It is apparent, therefore, that the exposure of tetraethyllead and tetraethyllead-containing compositions to any or all of the above environments results in a number of operational difficulties, including loss of antiknock effectiveness, carburetion difficulties such as the clogging of jets, filters, screens and the like resulting from the formation of sludge, gum and other types of sediment, as well as the above-described effects upon the color of the identified antiknock fluids.

The prior art contains many proposals whereby one or more of these difficulties may be obviated, but these have not proved very satisfactory because of the inherent complexity of the problem. For example, although many antioxidants have been developed which satisfactorily protect oxygen-sensitive fuels, oils and other inherently unstable organic hydrocarbons against atmospheric deterioration, such antioxidants almost without exception are unsatisfactory for the protection of organolead compounds and organolead-containing compositions.

When organolead-containing compositions are utilized in internal combustion engines other difficulties are frequently encountered. As indicated previously, antiknock fluids are provided with corrective agents or scavengers so as to effectively reduce the amount of metallic deposits in the engine by forming volatile metallic compounds which emanate from the engine in the exhaust gas stream. However, notwithstanding the high degree of efficiency of such scavengers the accumulation of engine deposits in combustion chambers and on engine parts such as pistons, valves, and the like cannot be entirely prevented. This accumulation of deposits is particularly prevalent when internal combustion engines are operated under conditions of low speed and light load. For example, when passenger cars, trucks, buses and the like are operated under conditions normally encountered in metropolitan localities the formation of excessive amounts of deposits frequently results. As a result of the notable improvements in fuel antiknock quality which have been made in recent years, such deposits present but a few minor problems in low compression engines. However, in recent years, there has been a marked trend in the automotive industry of utilizing high compression engines in passenger cars and struck. It has been found that the increase in compression ratios results in increased engine efficiency whereby the motoring public is provided with both greater power availability and greater economy of operation. However, with such high compression internal combustion engines the accumulation of deposits results in a number of serious problems, including increased detonation, deposit-induced autoignition or wild ping, spark plug fouling, reduction in exhaust valve life, and the like.

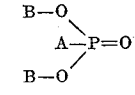
Ordinary detonation in the internal combustion engine has been defined as the spontaneous combustion of an appreciable portion of the charge, which results in an extremely rapid local pressure rise and produces a sharp metallic knock. The control of ordinary detonation may be effected by retarding ignition timing, by operating under part throttle conditions, by reducing the compression ratio of the engine and by using fuels having high antiknock qualities; that is, by using an organolead-containing fuel. Deposit-induced autoignition may be defined as the erratic ignition of the combustible charge by combustion chamber deposits resulting in an uncontrolled combustion and isolated bursts of audible and inaudible manifestations of combustion somewhat similar to knocking. Aside from the nuisance experienced by the passenger car operator, deposit-induced autoignition or wild ping often produces deleterious effects inasmuch as it is a precursor of preignition. Therefore, wild ping results in rough engine operating conditions with the attendant reduction in power output, and very often increased the wear of engine parts, piston burning and the like. In contrast to ordinary detonation, deposit-induced autoignition or wild ping cannot be satisfactorily controlled by retard-

ing ignition timing, nor by operating under part throttle conditions. Inasmuch as automotive engineers are desirous of utilizing in internal combustion engines the highest compression ratios permitted by the commercially available fuels, the reduction of compression ratios to eliminate this problem is not desirable nor feasible. Indeed, it is the consensus of opinion among the designers of internal combustion engines that engine developments have heretofore been greatly hindered by the limitations imposed by deposit-induced autoignition. It is evident, therefore, that the present requirement for fuel having high antiknock qualities shall be greatly surpassed by future requirements. Notwithstanding attempts to attain these qualities by alternative means, it is entirely probable that the most satisfactory method for the attainment of high octane fuels shall continue to be the use of antiknock agents, particularly of the organolead type. Although, as indicated, detonation can successfully be obviated by the use of organolead antiknock agents such as tetraethyllead, it has been found that the severity of the wild ping problem often increases with the octane quality of the fuel. Hence, the automotive industry is faced with the dilemma resulting from the fact that each time the octane quality of the fuel is raised to coincide with increases in compression ratio, deposit-induced autoignition generally becomes more severe. As a result, there is a paramount need existing for a new and improved method for altering the physical and chemical characteristics of deposits and for modifying the combustion process such that the detrimental effects of deposit-induced autoignition can be markedly suppressed or be eliminated.

Another serious problem directly attributed to the presence of engine deposits is spark plug failure, commonly termed "spark plug fouling." This deleterious effect results from the formation of conductive deposits on the firing end of spark plugs which provide a conductive surface for the electrical charge such that the decrease in resistance results in an insufficient potential across the spark plug electrodes. Under such circumstances, the production of a spark at the spark gap is prevented. To alleviate such spark plug failures, it has been proposed in the prior art to utilize certain additives in leaded fuel so as to alter the nature of the deposits formed on the spark plugs. In some cases, such additives have been shown to be rather effective for this purpose. However, despite the preponderate teaching of the prior art that satisfactory engine operation can be effected by such compositions, it has been found that the alleviation of spark plug failure is generally attained at the expense of both exhaust valve life and destructiveness of the organolead antiknock agent. The first of these problems, namely the reduction in exhaust valve life, is ultimately the result of exhaust valve burning and corrosion which are promoted by utilizing many of the materials proposed in accordance with the teachings of the prior art. More particularly, this reduction in exhaust valve life is a reduction in the length of time during which the valve operates without either excessive leakage or mechanical failure evidenced in extreme cases by the separation of the valve head from its stem. Such effects in turn result from corrosion and/or burning which terms are defined respectively as the weight loss of the total valve, which is most likely to occur in the head and throat area of the valve and the local removal of metal from the valve face resulting in valve leakage. The second type of difficulty resulting from the use of many of the additives suggested in the prior art, to wit the reduction in the effectiveness of the organolead antiknock agent, is frequently termed tetraethyllead destructiveness. That is to say, many of the additives suggested in the prior art exhibit a considerable degree of antagonism toward organolead antiknock agents such that there is a considerable degree in the reduction of the octane quality for which purpose the antiknock agent is employed. It is apparent, therefore, that the need exists for methods of obviating spark plug failures without incurring a reduction in exhaust valve life and organolead destructiveness.

It is therefore an object of the present invention to provide adjuvants for organolead compounds. It is likewise an object of this invention to provide means of improving compositions containing organolead antiknock agents such as antiknock fluids and antiknock fuels. Similarly, the provision of improved organolead compounds is another object of this invention. Furthermore, an object of this invention is to provide improved organolead-containing antiknock fluids and fuels. A particular object of this invention is to provide improved tetraethyllead and tetraethyllead-containing antiknock fluids. In addition, an object of this invention is to provide methods of improving antiknock fluids such that during compounding, storage and blending operations such materials are stabilized against the adverse effects of deteriorative environments. An additional object of the instant invention is to provide means of obviating deposit-induced autoignition, spark plug fouling and other secondary problems associated with the use of organolead-containing compositions. Other important objects of this invention will be apparent from the discussion hereinafter.

It has now been found that the above and other objects of this invention are attained by providing compositions of matter adapted for use as additives to fuel for spark fired internal combustion engines comprising an organolead antiknock agent and, in quantity sufficient to stabilize or improve said agent, a hydrocarbon-substituted phosphonate containing a total of from 8 to about 30 carbon atoms in the molecule. Such phosphorus compounds which are diesters of hydrocarbon-substituted phosphonic acids can be represented by the general formula



wherein A and B are hydrocarbon groups as defined hereinafter.

Considering first the hydrocarbon group of the above-described substituted phosphonates designated as A, it has been found efficacious to utilize a radical selected from the group consisting of alkyl containing from 1 to about 10 carbon atoms, cycloalkyl containing up to about 8 carbon atoms, and aryl containing from 6 to about 10 carbon atoms. It is apparent, therefore, that the diesters of hydrocarbon-substituted phosphonic acids utilized as organolead adjuvants in accordance with this invention can be diesters of certain alkyl, cycloalkyl, and aryl-substituted phosphonic acids. The alkyl-substituted embodiments are formed when A in the above general formula is a radical such as methyl, ethyl, n-propyl, isopropyl, and likewise the various straight and branched chain isomers of butyl, amyl, hexyl, heptyl, octyl, and like radicals up to and including about decyl. Similarly, in the embodiments of the adjuvants of this invention wherein A is a cycloalkyl group such a group is exemplified by the cyclohexyl radical which can be further substituted in any of the various positions with a methyl or ethyl radical. Generally speaking, however, the diesters of aryl-substituted phosphonic acids comprise a preferred embodiment of the adjuvants of this invention, such materials preferably containing a phenyl substituent which in turn can be substituted with 1 or 2 alkyl radicals. In such a case, however, it has been found that it is desirable to utilize phenyl radicals substituted with one or two alkyl groups, the total carbon atoms of which do not exceed about 4. Illustrative examples of such aryl groups include phenyl, o-methylphenyl, m-methylphenyl, p-methylphenyl, 2,4-dimethylphenyl, 3-propylphenyl, 4-ethylphenyl, 4-butylphenyl, 3,5-diethylphenyl and the like. In some instances the phenyl radi-

cals substituted in the ortho or para positions are preferred, particularly in the ease of formation of the corresponding phosphorus compound. In contrast, however, it is frequently of advantage to utilize the meta-substituted phenyl radicals because of the tendency of such a group of lowering the melting point of the final compound.

The hydrocarbon substituents designated hereinabove as B of the diesters of the hydrocarbon-substituted phosphonic acids utilized in accordance with the present invention can be selected from the group consisting of alkyl containing from 1 to about 12 carbon atoms, cycloalkyl containing up to about 10 carbon atoms and aryl containing from 6 to about 10 carbon atoms. Although satisfactory results are obtainable utilizing mixed diesters of hydrocarbon-substituted phosphonic acids, that is, compounds wherein the groups designated hereinabove as B are different, it is preferable, particularly from the standpoints of ease and economies of preparation, to select the compounds wherein the B radicals are the same at least insofar as the type of radicals are concerned. To illustrate, a preferred embodiment of this invention comprises dialkyl esters of hydrocarbon-substituted phosphonic acids wherein the alkyl groups contain from 1 to about 12 carbon atoms as indicated hereinbefore. Of such materials those containing two identical alkyl groups are the easiest to prepare and hence are the most readily available adjuvants for use in accordance with this invention. However, it will be appreciated that in the manufacture of such materials it is frequently possible to utilize mixtures of starting alkyl-substituted alcohols whereby the groups designated by B can be different within the alkyl family. The cycloalkyl esters, typical of an additional embodiment of the present invention are exemplified by the cyclohexyl radical and likewise substituted cyclohexyl radicals wherein one or more of the carbon atoms in the ring can be substituted with members of the lower alkyl series. As in the case of the group designated hereinbefore as A, the aryl esters of hydrocarbon-substituted phosphonic acids are compounds wherein the groups represented by B are preferably phenyl radicals which can be substituted with alkyl groups totaling no more than about four carbon atoms.

Typical diesters of hydrocarbon-substituted phosphonic acids as above defined are illustrated by such compounds as dimethyl benzene phosphonate, diethyl benzene phosphonate, dibutyl benzene phosphonate, di-n-amyl benzene phosphonate, di-(2-ethylhexyl)-benzene phosphonate, dicyclohexyl benzene phosphonate, di-p-tolyl benzene phosphonate, diethyl-4-methyl benzene phosphonate, ethylpropyl butane phosphonate, diphenyl propane phosphonate, dibutyl cyclohexane phosphonate, ethylisobutyl hexane phosphonate, and like materials. The methods for the preparation of the aforementioned type of phosphorus compounds will be familiar to one skilled in the art, the processes generally involving the interaction between a phosphorus halide or phosphorus oxyhalide and the corresponding alcohol. For further details regarding the preparation of such trihydrocarbon-substituted phosphonates, see Kosolapoff, "Organo Phosphorus Compounds." A facet of this invention is the fact that many of the previously described phosphonates are available as articles of commerce, frequently in the form of mixtures, and for this reason it is unnecessary to utilize substantially pure materials provided, however, that the above criteria are met.

The organolead antiknock agent utilized in the compositions of matter of the present invention consists of an organolead compound in which lead is directly bonded to carbon atoms. Such compounds are exemplified by the lead aryls such as tetraphenyllead, and the lead alkyls such as tetramethyllead, tetraethyllead, tetrapropyllead, tetrabutyllead, dimethyldiethyllead, methyltriethyllead, and the like, as well as mixtures of such compounds. Because of the generally superior characteristics of tetraethyllead and the ready accessibility thereof as an article of commerce, it constitutes a preferred embodiment of the organolead antiknock agent utilized in accordance with the present invention.

With the various compositions within the scope of the present invention the proportion of the tri-hydrocarbon-substituted phosphonate containing a total of from 8 to about 30 carbon atoms in the molecule utilized in conjunction with an organolead compound is such that there is a total of from between about 0.05 to about 0.80 theory of phosphorus. In this regard, a theory of phosphorus is defined as the amount of phosphorus theoretically required to react with the lead to form lead ortho phosphate, which quantity is two atoms of phosphorus per three atoms of lead. Thus, a theory of phosphorus corresponds to a phosphorus-to-lead atom ratio of 2:3 and the phosphorus-to-lead atom ratios utilized in the practice of this invention range from about 0.1:3 to about 1.6:3. This latter range corresponds to a range of from between about 0.05 to about 0.80 theory of phosphorus. However, generally speaking, it is sufficient to employ an amount of the previously described phosphonates such that there is an amount of phosphorus between about 0.1 and about 0.5 theory of phosphorus with the best overall results being obtained with amounts of about 0.1 to about 0.3 theory of phosphorus. The last-mentioned concentrations constitute a preferred embodiment of this invention.

Regarding many of the problems frequently associated with high octane quality fuel, an anomalous situation obtains. On one hand an effective adjuvant for organolead compounds should possess stability against deterioration in common environments, compatibility with the chemical entities with which it comes in contact, and volatility so as to possess the characteristic frequently referred to as engine inductibility. On the other hand, the mere selection of a phosphorus compound to acquire the optimum characteristics enumerated above does not necessarily assure the effectiveness of the compound in combatting such phenomena as spark plug fouling, wild ping and the like. It is entirely probable that some empirical relationship between physical properties and effectiveness in the obviation of such problems exists, but as yet the state of the art does not contain a satisfactory relationship of this type. However, the phosphorus materials within the purview of this invention for the most part possess the requisite physical properties adapting them for use as organolead adjuvants and at the same time are effective in obviating engine problems of the type described hereinbefore.

It will be apparent that there exists a number of variations in employing the adjuvants of this invention. For example, a facet of this invention involves the provision of a mixture of an organolead antiknock agent such as a lead alkyl and a diester of a hydrocarbon-substituted phosphonic acid containing from 8 to about 30 carbon atoms in the molecule of the type as described above. In such a case the resulting composition can be blended with hydrocarbon fuel of the gasoline boiling range to provide an improved fuel composition which under certain circumstances does not require the utilization of an organic halogen-containing material as a scavenger. It is believed that under these conditions the presence of a quantity of phosphorus as above described and chemically bonded in accordance with the requirements of the phosphonates used in this invention contributes sufficient scavenging action such that the amount of deposition in the engine is suitably controlled, notwithstanding the fact that lead phosphates generally have high melting points. Likewise, in this embodiment of the instant invention the general storage characteristics of organolead compounds are frequently enhanced.

Of perhaps more practical importance is a second variant of this invention, namely the utilization of the aforementioned diesters of hydrocarbon-substituted phos-

phonic acids in organolead containing antiknock fluids. It is well known in the art that the most convenient means of marketing and blending organolead antiknock agents is in the form of an antiknock fluid which usually contains, in addition to the lead compound, one or more organic bromine and/or chlorine compounds and an organic dye for identification purposes. On occasion such antiknock fluids likewise contain minor proportions of diluents, antioxidants, metal deactivators and the like. In line with the foregoing, therefore, a preferred embodiment of this invention involves providing improved antiknock fluids containing the requisite concentration of the above described phosphonates. Such improved antiknock fluids generally do not require the presence of a solubilizing agent or a stabilizer since the phosphorus compound itself is generally sufficiently miscible with the constituents of the antiknock fluid and imparts thereto a degree of stabilization. However, under some conditions additional benefits are to be derived by employing in the improved antiknock fluids of this invention the necessary quantities of such materials.

Still another variant of the present invention consists of providing improved fuel compositions. These normally consist of hydrocarbons of the gasoline boiling range containing a minor proportion of the aforesaid antiknock fluids of the present invention. It will be appreciated that the quantity of the antiknock fluid of the present invention utilized in my improved fuel compositions is primarily contingent upon the use for which the gasoline is intended. That is to say, when the fuel is intended for use in automotive engines such as passenger cars, trucks, buses and the like, an amount of any of my improved antiknock fluids equivalent to a lead content in the gasoline of from between about 0.53 and about 3.17 grams of lead per gallon is satisfactory. Thus, in the embodiments of this invention wherein I employ tetraethyllead as an antiknock agent such concentrations are equivalent to from between about 0.5 and about 3 milliliters of the compound per gallon. With the advent of the more recent high compression ratio internal combustion engines, however, it is becoming increasingly apparent that benefits are to be derived by employing somewhat greater concentrations of the organolead material in automotive gasolines. On this basis, therefore, automotive fuels containing up to about 4.75 grams of lead per gallon are contemplated. In contrast, when the improved antiknock fluids of the present invention are utilized in fuel for aviation engines somewhat higher concentrations are employed. Generally speaking, amounts of lead up to about 6.34 grams of lead per gallon can be utilized although somewhat lesser quantities are presently in vogue. In other words, in the tetraethyllead-containing embodiments of this invention there can be present up to about 6 milliliters of tetraethyllead per gallon as an improved antiknock fluid of my invention. Concentrations above these limits can be employed in both motor and aviation fuels, practical considerations being the prime criterion for establishing the upper concentration limit. As indicated hereinabove in all of the compositions of the present invention the amount of phosphorus is fixed within the limits above described. Thus, in the preferred fuel embodiments of my invention there is present an amount of phosphorus as a trihydrocarbon-substituted phosphonate wherein the number of carbon atoms in the molecule is from between 8 to about 30, such that there is from about 0.1 and 0.3 theory of phosphorus. In preparing the improved fuel compositions of this invention it is usually necesssary only to add the requisite quantity of the improved fluid to the fuel and by means of stirring, shaking or other means of physical agitation homogeneous fuel compositions are provided. Although the simplest means of preparing such fuels is to blend therewith the necessary quantity of an improved antiknock fluid of this invention it is possible to add a conventional antiknock fluid to the fuel and subsequently blend therewith the necessary quantity of the trihydrocarbon-substituted phosphonate. In addition to reversing this order of addition of conventional antiknock fluids and trihydrocarbon substituted phosphonates, another variant within the purview of this invention is to blend with the fuel each of the individual constituents of my antiknock fluids separately.

To illustrate the effectiveness of the improved antiknock fluids of the present invention consideration was given to the problem of spark plug fouling. In order to do this, recourse was made to the following general test procedure utilizing a standard modern V–8 engine equipped with overhead valves having a 3¾" bore, a 3 7/16" stroke, a 303.7 cubic inch displacement and a compression ratio of 7.25 to 1 equipped with commercially available spark plugs. In order to establish a base line this engine was operated in conjunction with an engine dynamometer on a standard commercial fuel containing 3 milliliters of tetraethyllead per gallon as a conventional antiknock fluid containing 0.5 theory of bromine as ethylene dibromide, and 1.0 theory of chlorine as ethylene dichloride. This engine was operated under a durability schedule used for spark plug deposit accumulation patterned after road conditions experienced in city driving which are known to produce spark plug fouling of the greatest magnitude. Such operation was substantially continuous until a number of spark plug failures was detected thereby establishing a quantitative measure of the degree of spark plug fouling which can be expressed in average hours to plug failure. The engine was then freed from deposits and equipped with new spark plugs. The same procedure was repeated using the same fuel base stock to which was added an improved antiknock fluid of the present invention. The following examples more specifically illustrate the beneficial effect attending the use of an improved antiknock fuel of this invention.

Example I

To 300 gallons of a petroleum hydrocarbon fuel available as an article of commerce was added 900 milliliters of etraethyllead in a fluid containing tetraethyllead, 0.5 theory of bromine as ethylene dibromide, and 1.0 theory of chlorine as ethylene dichloride. The resulting blend was intimately mixed producing a homogeneous fuel composition containing 3.0 milliliters of tetraethyllead per gallon. The standard V–8 engine described hereinbefore was then operated on this fuel composition until a spark plug failure was detected. At this time the engine was shut down and the fouled spark plug was removed and replaced with a new spark plug. The engine was then operated in the same manner until a second plug failure was detected at which time the engine was shut down and the fouled plug was removed and replaced with a new one. This procedure was repeated until a third spark plug failure was produced. It was found that the average time to the three spark plug failures was 36 hours. The entire procedure was then repeated twice more with the same engine and the same fuel composition and it was found that the average time to spark plug fouling amounted to 32 and 33 hours of engine operation. Therefore, the average time to spark plug failures amounted to 34 hours.

Example II

To 1000 gallons of the same fuel base stock was added 3 liters of tetraethyllead as a fluid comprising 0.5 theory of bromine as ethylene dibromide, 1.0 theory of chlorine as ethylene dichloride, and 0.2 theory of phosphorus as dibutyl benzene phosphonate. The resulting blend was then intimately mixed producing a homogeneous fuel composition containing 3.0 milliliters of tetraethyllead per gallon. The engine was then operated on this fuel composition and it was found that three spark plug failures

had not occurred after 167 hours of operation. Thus, the improvement in spark plug performance produced by the utilization of an improved fuel of the present invention amounted to an increase of at least 492 percent of the base line.

As the data shown in the above examples indicate, the utilization of a di-hydrocarbon ester of a hydrocarbon substituted phosphonic acid containing a total of from 8 to about 30 carbon atoms in the molecule results in a considerable increase in spark plug performance. Comparable effectiveness is similarly obtained when other improved compositions of the present invention are utilized for the attainment of the objectives as set forth hereinbefore. When such adjuvants as ethylisobutyl hexane phosphonate, di-n-amyl benzene phosphonate, di-(2-ethylhexyl)-benzene phosphonate, dicyclohexyl benzene phosphonate, and diphenyl propane phosphonate, are utilized in accordance with the present invention comparable effectiveness regarding minimization of spark plug fouling is obtained. In contrast, when certain phosphonates not meeting the characteristics previously set forth are employed a lesser degree of effectiveness obtains. Without desiring to be found by the following explanation regarding the enhanced effectiveness of the adjuvants of this invention, a tenable explanation apparently involves a proper balance between physical properties such as stability, volatility, solubility, compatibility and the like, and the energy relationships or ease of decomposition which may attribute to the overall effectiveness of the compound by facilitating decomposition at the proper instant in the engine cycle.

An additional important advantage obtained from practicing the instant invention is the fact that for the most part the trihydrocarbon substituted phosphonates containing a total of from between 8 to about 30 carbon atoms in the molecule used as organolead adjuvants have little or no antagonistic effect upon the antiknock agent generally used in the fuel. That is to say, the antagonism exhibited by a compound such as dibutyl benzene phosphonate toward organolead antiknock agents is considerably lower than might be expected despite statements in the literature to the effect that phosphorus material in general are the most serious antagonists toward tetraethyllead. In line with the enhanced effectiveness of such adjuvants this surprising benefit regarding a minimum of organolead destructiveness is perhaps associated with the degree of oxidation stability inherent in trihydrocarbon substituted phosphonates utilized in accordance with this invention. In other words, it is not inconceivable that the adjuvants of this invention are capable of decomposing at the proper instant in the engine cycle so as to exhibit the beneficial effects regarding deposit induced engine problems while at the same time decomposing at a time during the cycle sufficiently far removed from the point at which the organolead compound exerts its beneficial antiknock activity.

By the use of the diverse improved organolead containing compositions of this invention other beneficial effects are obtained. For example, when operating an internal combustion engine on an improved fuel of the present invention a marked diminution in wild ping results. As in the case of the obviation of other deposit induced problems it is preferred to utilize the adjuvants of this invention in high octane quality fuel because of the fact that most of such problems exist on combustion of such fuels.

Because of their adaptability the adjuvants of the present invention can be successfully utilized with any of the wellknown organolead antiknock agents as indicated hereinbefore. Likewise, insofar as the halide scavengers are concerned, the trihydrocarbon substituted phosphonates used in this invention can be employed in antiknock fluids and fuels containing such materials as ethylene dibromide, ethylene dichloride, mixed dibromotoluenes, trichlorobenzenes, and in general, such organic halide scavengers as those disclosed in U.S. 1,592,954; 1,668,022; 2,364,921; 2,398,281; 2,479,900; 2,479,901; 2,479,902; 2,479,903; and 2,496,983. Likewise, the adjuvants of this invention can be used in conjunction with other well known motor fuel adjuvants such as antioxidants, organolead stabilizers, organic dyes, solubilizers, and indeed with other catalytically active materials frequently employed in fuel.

Having fully described the nature of the present invention, the need therefor, and the best mode devised for carrying it out, it is not intended that this invention be limited except within the spirit and scope of the appended claims.

I claim:

1. Improved fuel for spark ignition internal combustion engines consisting essentially of gasoline, from about 0.53 to about 6.34 grams of lead per gallon as an organolead antiknock agent, a scavenging amount of organic halide material capable of reacting with lead during combustion in a spark ignition internal combustion engine to form relatively volatile lead salts containing halogen, and a dialkyl benzene phosphonate, said benzene phosphonate having benzene bonded directly to phosphorus, said alkyl groups containing from one to about four carbon atoms, said phosphonate being present in said fuel in amount such that the phosphorus-to-lead atom ratio is from about 0.1:3 to about 1.6:3.

2. Improved fuel for spark ignition internal combustion engines consisting essentially of gasoline, from about 0.53 to about 6.34 grams of lead per gallon as an organolead antiknock agent, a scavenging amount of organic halide material capable of reacting with the lead during combustion in a spark ignition internal combustion engine to form relatively volatile lead salts containing halogen and dibutyl benzene phosphonate present in amount such that the phosphorus-to-lead atom ratio is from about 0.1:3 to about 1.6:3.

3. A composition of matter adapted for use as an additive to gasoline consisting essentially of an organolead antiknock agent, a scavenging amount of organic halide material capable of reacting with lead during combustion in a spark ignition internal combustion engine to form relatively volatile lead salts containing halogen, and a dialkyl benzene phosphonate, said benzene phosphonate having benzene bonded directly to phosphorus, each said alkyl groups containing from one to about four carbon atoms, said phosphonate being present in said composition in amount such that the phosphorus-to-lead atom ratio is from about 0.1:3 to about 1.6:3.

4. A composition adapted for use as an additive to gasoline, said additive consisting essentially of tetraethyllead, an organic halide scavenger consisting essentially of 0.5 theory of bromine as ethylene dibromide and 1.0 theory of chlorine as ethylene dichloride based on the lead, and dibutyl benzene phosphonate present in amount such that the phosphorus-to-lead atom ratio is from about 0.1:3 to about 1.6:3.

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