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ANTIKNOCK FLUIDS

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The instant invention relates to improved antiknock fluids which, when blended with liquid hydrocarbon fuels, provide fuel compositions of superior performance qualities which are particularly effective in suppressing or eliminating deposit induced autoignition.

In recent years there has been a marked trend in the automotive industry of utilizing internal combustion engines having high compression ratios in passenger cars and trucks. It has been found that this 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. High compression engines almost uniformly require fuels of high octane number for most efficient operation. Of the several methods for raising the octane number of gasoline developed to date, that of utilizing an antiknock compound such as tetraethyllead has been most successful. Although such antiknock agents have been provided with corrective agents, commonly known as scavengers, which effectively reduce the deposition of metallic deposits in the engine by forming volatile metallic compounds which emanate from the engine in the exhaust gas stream, the accumulation of engine deposits in combustion chambers and on other engine parts such as pistons, valves, and the like, cannot be entirely prevented, particularly when the vehicles are operated under conditions of low speed and light load, as encountered in metropolitan localities. 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, whereas with engines of higher compression ratios two more serious problems are becoming increasingly prevalent, those of detonation and deposit induced autoignition or "wild ping."

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. Deposit induced autoignition may be defined as the erratic ignition of the combustible charge by combustion chamber deposits, resulting in uncontrolled combustion and isolated bursts of audible 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 which produces harmful effects in the engine such as increased 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 retarding 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 deposit induced autoignition is not desirable nor feasible. It is evident, therefore, that the present requirement for fuels having antiknock qualities shall be equalled or surpassed by the requirement of the future; and 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. Consequently, there is a paramount need existing for a new and improved method for decreasing the amount of deposit formation, for altering the thermal properties of such deposits in a beneficial manner, and for modifying the combustion process such that the detrimental effects of deposit induced autoignition or "wild ping" may be markedly suppressed or be eliminated.

Accordingly, it is an object of this invention to provide improved fluids for gasoline which concurrently prevent detonation or knocking and obviate the deleterious effects of deposit induced autoignition or "wild ping." It is a further object of this invention to provide additives for leaded fuels which suppress or eliminate deposit induced autoignition or "wild ping." An additional object of this invention is to provide additives to gasoline which suppress or eliminate the detrimental effects of deposits previously accumulated in an engine. Additional important objects of this invention will become apparent from the discussion which follows.

We have found that the above and other objects of this invention can be accomplished by adding to gasoline an improved antiknock fluid comprising an organolead antiknock agent, and a gasoline soluble organic lithium material.

The gasoline soluble organic lithium materials we employ in our improved antiknock compositions include such substances as lithium chelates, lithium porphines, lithium phthalocyanines, lithium amides, and lithium mercaptides.

Lithium chelates, in general, consist of two types, both of which we can employ in our improved antiknock compositions. The first type comprises lithium derivatives of β-diketones, β-diketonic esters, o-hydroxy-aromatic esters and aldehydes, o-nitrophenols, and the like, which derivatives are sometimes referred to as simple lithium derivatives and which exhibit both polar and non-polar properties. We have found that such lithium derivatives possess non-polar properties sufficient to impart solubility in gasoline. Thus, the gasoline soluble organic lithium compounds we employ in our improved antiknock fluids can be lithium derivatives of such substances as, for example, acetoacetic esters, acetylacetone, benzoylacetone, o-nitrophenol, 3-nitro-o-cresol, quinizarin, diesters of malonic acid, diesters of substituted malonic acid, cyanoacetic esters, 1-ketohydrindene-2-carboxylic esters, and esters of ethanetetracarboxylic acid.

The second type of lithium chelates which we employ in our improved antiknock fluids comprises lithium 4-covalent compounds; that is, coordinate compounds of lithium wherein lithium has a covalency number of four. Thus, the lithium atom is linked to complexing atoms through four covalent or coordinate covalent bonds; that is, in such compounds lithium is directly linked to four other atoms. Such compounds which are, in general, highly stable and are gasoline soluble, are sometimes prepared from the same compounds as the first type of lithium derivatives, but differ to the extent that addition compounds are formed, either with the original or some similar organic compound, or by the coordination of two single molecules such as of water, forming, for example, coordinated dihydrated lithium compounds. Thus, the gasoline

soluble organic lithium compounds we employ in our improved antiknock fluids can be lithium derivatives of such compounds as, for example, benzoylacetone, methyl salicylate, salicylaldehyde, quinizarin, and ψ-indoxylspirocyclopentane. Thus, we can employ derivatives such as those which have been characterized as lithium benzoylacetone dihydrate, lithium methyl salicylate dihydrate, lithium salicylaldehyde dihydrate, lithium coordinated with two molecules of salicylaldehyde, lithium coordinated partially with quinizarin and with a molecule of salicylaldehyde, lithium coordinated with two molecules of 4-indoxyspirocyclopentane, and the like.

Lithium porphines are complex derivatives of porphins which are fundamentally heterocyclic structures consisting of four pyrrole rings united by methylene groups, the hydrogens of which can be substituted with organic radicals. Thus, the gasoline soluble organic lithium compounds we employ in our improved antiknock fluids can be lithium derivatives of porphins, wherein the α, β, γ, and δ carbon atoms are substituted with radicals which can be the same or different and are selected from the class consisting of hydrogen, alkyl, and aryl radicals.

Lithium phthalocyanines are complex derivatives of the phthalocyanines which are heterocyclic structures containing four isoindole rings linked in a 16-membered ring of alternate carbon and nitrogen atoms around a central atom. Thus, the gasoline soluble organic lithium compounds we employ in our improved antiknock fluids can be lithium derivatives of the phthalocyanins such as, for example, dilithium phthalocyanine.

Lithium amides can be lithium derivatives of primary and secondary amines. Thus, the gasoline soluble organic lithium compounds we employ in our improved antiknock fluids can be lithium amides of primary amines such as, for example, methylamine, ethylamine, phenylamine, and the like; that is, the lithium amides can be, respectively, lithium methylamide, lithium ethylamide, lithium phenylamide, and the like. In addition, the lithium compounds of our improved antiknock fluids can be lithium amides of secondary amines such as, for example, dimethylamine, diphenylamine, methylphenylamine, and the like; that is, the lithium amides can be, respectively, lithium dimethylamide, lithium diphenylamide, lithium methylphenylamide, and the like.

Lithium mercaptides are lithium derivatives of alkyl and aryl mercaptans and are characterized by a lithium-to-sulfur bond. Thus, the gasoline soluble organic lithium compounds we employ in our improved antiknock fluids can be lithium derivatives of such mercaptans as, for example, methylmercaptan, ethylmercaptan, N-propylmercaptan, isopropylmercaptan, phenylmercaptan, 1,2-ethanedithiol, and the like.

An advantage of the gasoline soluble organic lithium compounds we employ in the improved antiknock compositions of our invention is the stability of such materials in the presence of moisture, air, or other gases such as carbon dioxide. This stability we attribute to the fact that such gasoline soluble organic lithium compounds are free from lithium-to-carbon bonds.

As stated heretofore, we employ gasoline soluble organic lithium materials in our improved antiknock compositions. As a preferred embodiment of the instant invention, we have found it efficacious to utilize organic lithium materials having a solubility of at least about 0.1 grams of lithium per gallon of gasoline. The precise solubility of the organic lithium materials we employ in our improved antiknock compositions is determined somewhat by the selection of the organic portion of such materials. Thus, when we desire appreciable gasoline solubility, we obtain this by the judicious selection of the organic portion of such materials. Thus, for example, we have found that, in general, the greater the organic portion of the organic lithium material, the greater is the hydrocarbon solubility. The aforementioned selection of the organic portion of these organic lithium materials we can employ in

our improved antiknock compositions is also contingent upon the type of fuel in which the improved antiknock fluids of our invention is to be utilized. In addition, we sometimes find it advantageous to employ solubilizing agents such as, for example, excess of an organic reactant used to prepare the gasoline soluble organic lithium compound, or conventional organic materials commonly utilized as solubilizing agents.

The general methods for the preparation of the gasoline soluble organic lithium compounds we employ in the improved antiknock compositions of our invention are well known to those skilled in the art. Specific literature references wherein such methods are described include J. Chem. Soc. 1931 pt. I, 361, wherein the lithium chelate compounds are discussed; J. Am. Chem. Soc. 70, 1808 (1948), wherein the lithium porphines are discussed; Proc. Natl. Inst. Sci., India, 13, 141 (1947), wherein the lithium phthalocyanins are discussed; and U. S. 2,141,058, wherein the lithium amides are discussed.

We have found that, in general, we can accomplish the objects of the instant invention by adding to an organolead antiknock agent, a gasoline soluble organic lithium material in amounts such that the lithium-to-lead atom ratio is in the order of between about 0.001 to 1 and about 10.0 to 1. A preferred embodiment of the instant invention involves adding to a conventional antiknock fluid comprising an organolead antiknock agent and a corrective agent or scavenger, a gasoline soluble organic lithium material in amounts such that the lithium-to-lead atom ratio is in the order of between about 0.5 to 1 and about 5.0 to 1. In compounding some of our improved antiknock fluids we have found that we can partially dissolve and partially disperse or suspend certain of the gasoline soluble organic lithium materials in conventional antiknock mixtures, thereby obtaining improved antiknock fluids having the desired lithium-to-lead atom ratios. Such improved antiknock fluids when blended and intimately mixed with liquid hydrocarbon fuels produce improved homogeneous fuel compositions which are effective in virtually eliminating deposit induced autoignition or "wild ping." The following examples more specifically illustrate the general methods for compounding the improved antiknock compositions of our invention.

Example I

To an amount of a conventional tetraethyllead antiknock mixture equivalent to about 3 milliliters of tetraethyllead was added about 0.95 gram of lithium octylacetoacetate having a lithium content of approximately 3.14 per cent by weight. The resulting blend was intimately mixed, producing a fluid containing the following percentages by weight of individual components: tetraethyllead, 58.9; ethylene dibromide, 17.1; ethylene dichloride, 18.0; lithium octylacetoacetate, 4.2; and inert ingredients, 1.8. When 8.4 grams of this fluid were dissolved and intimately mixed with 1 gallon of a petroleum hydrocarbon fuel, the resulting homogeneous fuel contained 3 milliliters of tetraethyllead per gallon and had a lithium-to-lead atom ratio of 0.103 to 1.

Example II

To an amount of a conventional tetraethyllead antiknock mixture equivalent to about 3 milliliters of tetraethyllead was added about 1.95 grams of lithium octylacetoacetate having a lithium content of approximately 3.14 per cent by weight. The resulting blend was intimately mixed, producing a fluid containing the following percentages by weight of individual components; tetraethyllead, 49.5; ethylene dibromide, 14.4; ethylene dichloride, 15.1; lithium octylacetoacetate, 19.5; and inert ingredients, 1.5. When 10.0 grams of this fluid were dissolved and intimately mixed with 1 gallon of a petroleum hydrocarbon fuel, the resulting homogeneous fuel contained 3 milliliters of tetraethyllead per gallon and had a lithium-to-lead atom ratio of 0.575 to 1.

Example III

To an amount of a conventional tetraethyllead antiknock mixture equivalent to about 3 milliliters of tetraethyllead was added about 4.45 grams of lithium octylacetoacetate having a lithium content of approximately 3.14 per cent by weight. The resulting blend was intimately mixed, producing a fluid containing the following percentages by weight of individual components: tetraethyllead, 39.5; ethylene dibromide, 11.5; ethylene dichloride, 12.1; lithium octylacetoacetate, 35.6; and inert ingredients, 1.3. When 12.6 grams of this fluid were dissolved and intimately mixed with 1 gallon of a petroleum hydrocarbon fuel, the resulting homogeneous fuel contained 3 milliliters of tetraethyllead per gallon and had a lithium-to-lead atom ratio of 1.32 to 1.

Example IV

To an amount of a conventional tetraethyllead antiknock mixture equivalent to about 3 milliliters of tetraethyllead was added about 2.8 grams of lithium octylacetoacetate having a lithium content of approximately 3.14 per cent by weight. The resulting blend was intimately mixed, producing a fluid containing the following percentages by weight of individual components: tetraethyllead, 45.6; ethylene dibromide, 13.3; ethylene dichloride, 13.9; lithium octylacetoacetate, 25.8; and inert ingredients, 1.4. When 10.9 grams of this fluid were dissolved and intimately mixed with 1 gallon of a petroleum hydrocarbon fuel, the resulting homogeneous fuel contained 3 milliliters of tetraethyllead per gallon and had a lithium-to-lead atom ratio of 0.830 to 1.

The foregoing specific examples are illustrative of the methods of compounding typical improved antiknock fluid and fuel compositions of the instant invention. It is not intended that our invention be limited to improved antiknock fluids of such proportions to provide 3 milliliters of tetraethyllead per gallon of fuel, for we have found that we can provide fluids in such proportions to provide amounts of tetraethyllead from between about 0.5 to about 6.0 milliliters per gallon of fuel.

To demonstrate the effectiveness of our improved antiknock compositions in suppressing or eliminating deposit induced autoignition or "wild ping," we subject both a hydrocarbon fuel treated in accordance with our invention and another portion of the same hydrocarbon fuel treated with a conventional antiknock mixture to a test procedure involving the use of a single-cylinder CFR knock test engine equipped with an L-head cylinder and a "wild ping" counter which records the total number of "wild pings" which have occurred during the test periods. Such apparatus includes an extra spark plug used as an ionization gap which is installed in a second opening in the combustion chamber. A mechanical breaker switch driven at camshaft speed is also provided which, when closed, makes the "wild ping" counter ineffective for the duration of the normal flame in the combustion chamber. The breaker is open for 80 crankshaft degrees between 70° BTC and 10° ATC. If a flamefront induced early in the cycle by deposits reaches the ionization gap during this open period, the counter registers a "wild ping," regardless of the audible manifestations. During normal combustion with ignition timing at TDC, the flamefront reaches the ionization gap at 15 to 18° ATC during the period wherein the points are closed, and no count is made. The actual test procedure consists essentially of operating a single-cylinder CFR knock test engine equipped with an L-head cylinder initially having a clean combustion chamber under relatively mild cycling conditions for deposit formation until an equilibrium with regard to deposit induced autoignition is reached. The effect of fuels treated in accordance with the instant invention is determined by comparing the test results obtained using the fuel treated with our improved antiknock fluids to those obtained using a fuel treated with a conventional antiknock mixture. Since the "wild ping" counter records the total number of "wild pings" which have occurred during the test procedures, a quantitative expression for the amount of deposit induced autoignition is the number of "wild pings" per hour of operation. The effectiveness of our improved antiknock compositions in virtually eliminating deposit induced autoignition will be apparent from the following specific examples.

Example V

To 1 gallon of a commercially available fuel was added an improved antiknock fluid in an amount equivalent to about 3 milliliters of tetraethyllead, which fluid comprised 61.5 parts by weight of tetraethyllead, 17.9 parts by weight of ethylene dibromide, 18.8 parts by weight of ethylene dichloride, 4.4 parts by weight of lithium octylacetoacetate, and 1.9 parts by weight of inert ingredients. The homogeneous treated fuel was then subjected to the test procedure described heretofore, and the results were compared with another portion of the same gasoline treated with 3 milliliters of tetraethyllead in an antiknock fluid comprising 61.5 parts by weight of tetraethyllead, 17.9 parts by weight of ethylene dibromide, 18.8 parts by weight of ethylene dichloride, and 1.9 parts by weight of inert ingredients. The fuel composition containing the improved antiknock fluid produced 85.8 "wild pings" per hour, whereas the identical fuel containing the conventional antiknock fluid produced 118.1 "wild pings" per hour. Thus, treatment of a petroleum hydrocarbon fuel with an improved antiknock composition of our invention resulted in a reduction of deposit induced autoignition of 27.3 per cent.

Example VI

To 1 gallon of a commercially available fuel was added an improved antiknock fluid in an amount equivalent to about 3 milliliters of tetraethyllead, which fluid comprised 61.5 parts by weight of tetraethyllead, 17.9 parts by weight of ethylene dibromide, 18.8 parts by weight of ethylene dichloride, 24.2 parts by weight of lithium octylacetoacetate, and 1.9 parts by weight of inert ingredients. The homogeneous treated fuel was then subjected to the test procedure described heretofore, and the results were compared with another portion of the same gasoline treated with 3 milliliters of tetraethyllead in an antiknock fluid comprising 61.5 parts by weight of tetraethyllead, 17.9 parts by weight of ethylene dibromide, 18.8 parts by weight of ethylene dichloride, and 1.9 parts by weight of inert ingredients. The fuel composition containing the improved antiknock fluid produced 31.9 "wild pings" per hour, whereas the identical fuel containing the conventional antiknock fluid produced 118.1 "wild pings" per hour. Thus, treatment of a petroleum hydrocarbon fuel with an improved antiknock composition of our invention resulted in a reduction of deposit induced autoignition of 73.0 per cent.

Example VII

To 1 gallon of a commercially available fuel was added an improved antiknock fluid in an amount equivalent to about 3 milliliters of tetraethyllead, which fluid comprised 61.5 parts by weight of tetraethyllead, 17.9 parts by weight of ethylene dibromide, 18.8 parts by weight of ethylene dichloride, 24.2 parts by weight of lithium octylacetoacetate, and 1.9 parts by weight of inert ingredients. The homogeneous treated fuel was then subjected to the test procedure described heretofore, and the results were compared with another portion of the same gasoline treated with 3 milliliters of tetraethyllead in an antiknock fluid comprising 61.5 parts by weight of tetraethyllead, 17.9 parts by weight of ethylene dibromide, 18.8 parts by weight of ethylene dichloride, and 1.9 parts by weight of inert ingredients. The fuel composition containing the improved antiknock fluid produced 26.5 "wild pings" per hour, whereas the identical fuel containing the conventional antiknock fluid produced 118.1 "wild pings" per hour. Thus, treatment of a petroleum hydrocarbon fuel

with an improved antiknock composition of our invention resulted in a reduction of deposit induced autoignition of 77.6 per cent.

Example VIII

To 1 gallon of a commercially available fuel was added an improved antiknock fluid in an amount equivalent to about 3 milliliters of tetraethyllead, which fluid comprised 61.5 parts by weight of tetraethyllead, 17.9 parts by weight of ethylene dibromide, 18.8 parts by weight of ethylene dichloride, 55.4 parts by weight of lithium octylacetoacetate, and 1.9 parts by weight of inert ingredients. The homogeneous treated fuel was then subjected to the test procedure described heretofore, and the results were compared with another portion of the same gasoline treated with 3 milliliters of tetraethyllead in an antiknock fluid comprising 61.5 parts by weight of tetraethyllead, 17.9 parts by weight of ethylene dibromide, 18.8 parts by weight of ethylene dichloride, and 1.9 parts by weight of inert ingredients. The fuel composition containing the improved antiknock fluid produced 27.4 "wild pings" per hour, whereas the identical fuel containing the conventional antiknock fluid produced 118.1 "wild pings" per hour. Thus, treatment of a petroleum hydrocarbon fuel with an improved antiknock composition of our invention resulted in a reduction of deposit induced autoignition of 76.8 per cent.

Example IX

To 1 gallon of a commercially available fuel was added an improved antiknock fluid in an amount equivalent to about 3 milliliters of tetraethyllead, which fluid comprised 61.5 parts by weight of tetraethyllead, 17.9 parts by weight of ethylene dibromide, 18.8 parts by weight of ethylene dichloride, 34.9 parts by weight of lithium octylacetoacetate, and 1.9 parts by weight of inert ingredients. The homogeneous treated fuel was then subjected to the test procedure described heretofore, and the results were compared with another portion of the same gasoline treated with 3 milliliters of tetraethyllead in an antiknock fluid comprising 61.5 parts by weight of tetraethyllead, 17.9 parts by weight of ethylene dibromide, 18.8 parts by weight of ethylene dichloride, and 1.9 parts by weight of inert ingredients. The fuel composition containing the improved antiknock fluid produced 36.8 "wild pings" per hour, whereas the identical fuel containing the conventional antiknock fluid produced 107.0 "wild pings" per hour. Thus, treatment of petroleum hydrocarbon fuel with an improved antiknock composition of our invention resulted in a reduction of deposit induced autoignition of 65.6 per cent.

The aforementioned specific examples are illustrative of the effectiveness of the gasoline soluble organic lithium materials we can employ in our improved antiknock compositions. As previously indicated, we can obtain comparable results by employing in our improved antiknock compositions amounts of gasoline soluble organic lithium materials such as lithium porphines, lithium phthalocyanines, lithium amides, lithium mercaptides, and other lithium chelates such that the lithium-to-lead atom ratio is of the order of magnitude described hereinbefore.

Although the laboratory test procedure described heretofore simulates engine conditions encountered under road operation, we have found that the laboratory instrumentation utilized in the test procedure is extremely sensitive and measures effects with more accuracy and precision than can be detected under road conditions. Thus, for satisfactory road operation we can utilize improved antiknock compositions which produce a reduction in deposit induced autoignition or "wild ping" in the order of approximately 70 per cent as determined by the laboratory test procedure. For other service, such as stationary engines and the like, compositions effecting less than this reduction are effective.

Without being bound to a theory of the startling effectiveness of our improved antiknock compositions, we believe that a tenable explanation of this effectiveness results from a combination of at least two concurrent effects. We believe that the presence of the organic lithium materials in our improved antiknock fluid compositions alters the oxidation process of the carbonaceous constituents of the combustion chamber deposits, thereby reducing the kinetic energy released by this oxidation to a point at which it is insufficient to initiate burning of the mixture. More specifically, we believe that deposit induced autoignition is produced by burning or glowing of deposits which in turn is an exothermic process promoted by the lead compounds present in the deposits. We feel that the organic lithium material in our improved antiknock compositions or products of combustion of the lithium material suppress the aforementioned catalytic action of the lead compounds by a poisoning mechanism. In addition, we believe that the organic lithium materials present in our improved antiknock compositions concurrently increase the thermal conductivity of such deposits by reducing their fusion temperatures, whereby the deposit is physically changed from a highly porous thermal insulator to a non-porous, more dense mass having superior heat conduction properties.

We have found that we can employ diverse lead antiknock compounds and organic halide corrective agents or scavengers with equal effectiveness to those specifically discussed heretofore. Thus, for example, we can employ various organolead antiknock agents as well as diverse corrective agents or scavengers such as, for example, those disclosed in U. S. Patents 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. In addition to the foregoing, we find that antioxidant compositions or stabilizers and organic dyes and the like can be successfully employed in our improved antiknock fluid compositions.

Many variations in the methods of employing our improved antiknock compositions within the spirit and scope of the instant invention will be apparent to those skilled in the art. As indicated heretofore, we have found that we can obtain comparable results by adding the organic lithium material directly to a gasoline previously treated with a conventional antiknock mixture.

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

We claim:

1. An antiknock composition consisting essentially of a lead alkyl antiknock agent and a gasoline soluble organic lithium compound which is free from lithium-to-carbon bonds, said compound being further characterized by (*a*) having a linking element between lithium and carbon, said element being selected from the group consisting of oxygen, nitrogen and sulfur, and (*b*) containing only elements selected from the group consisting of lithium, carbon, hydrogen, oxygen, sulfur and nitrogen; and organic lithium compound being present in amount such that the lithium-to-lead atom ratio is between about 0.001 to 1 and about 10.0 to 1.

2. An antiknock composition consisting essentially of tetraethyllead and a gasoline soluble organic lithium compound which is free from lithium-to-carbon bonds, said compound being further characterized by (*a*) having a linking element between lithium and carbon, said element being selected from the group consisting of oxygen, nitrogen and sulfur, and (*b*) containing only elements selected from the group consisting of lithium, carbon, hydrogen, oxygen, sulfur and nitrogen; said organic lithium compound being present in amount snch that the lithium-to-lead atom ratio is between about 0.001 to 1 and about 10.0 to 1.

3. An antiknock composition consisting essentially of tetraethyllead and a gasoline soluble organic lithium compound which is free from lithium-to-carbon bonds, said

compound being further characterized by (*a*) having a linking element between lithium and carbon, said element being selected from the group consisting of oxygen, nitrogen and sulfur, and (*b*) containing only elements selected from the group consisting of lithium, carbon, hydrogen, oxygen, sulfur and nitrogen; said organic lithium compound being present in amount such that the lithium-to-lead atom ratio is between about 0.5 to 1 and about 5.0 to 1.

4. Gasoline containing from between about 0.5 to about 6.0 milliliters of tetraethyllead per gallon and a gasoline soluble organic lithium compound which is free from lithium-to-carbon bonds, said compound being further characterized by (*a*) having a linking element between lithium and carbon, said element being selected from the group consisting of oxygen, nitrogen and sulfur, and (*b*) containing only elements selected from the group consisting of lithium, carbon, hydrogen, oxygen, sulfur and nitrogen; said organic lithium compound being present in amount such that the lithium-to-lead atom ratio is between about 0.001 to 1 and about 10.0 to 1.

5. The composition of claim 2 further characterized in that said organic lithium compound is a lithium chelate compound.

6. The composition of claim 2 further characterized in that said organic lithium compound is a lithium porphine compound.

7. The composition of claim 2 further characterized in that said organic lithium compound is a lithium phthalocyanine compound.

8. The composition of claim 2 further characterized in that said organic lithium compound is a lithium amide.

9. The composition of claim 2 further characterized in that said organic lithium compound is a lithium mercaptide.

10. The composition of claim 4 further characterized in that said organic lithium compound is a lithium chelate compound.

11. The composition of claim 4 further characterized in that said organic lithium compound is a lithium porphine compound.

12. The composition of claim 4 further characterized in that said organic lithium compound is a lithium phthalocyanine compound.

13. The composition of claim 4 further characterized in that said organic lithium compound is a lithium amide.

14. The composition of claim 4 further characterized in that said organic lithium compound is a lithium mercaptide.

15. The composition of claim 4 further characterized in that said organic lithium compound is a lithium chelate formed with a β-diketonic ester.

16. Gasoline containing from between about 0.5 to about 6.0 ml. of tetraethyllead per gallon and lithium octylacetoacetate present in amount such that the lithium-to-lead atom ratio is between about 0.5 to 1 and about 5.0 to 1.

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